UNIFORMED SERVICES UNIVERSITY OF THE HEALTH SCIENCES

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15 JUNE 2005

APPROVAL SHEET

Title of Thesis: **"Detection Levels of Drinking Water Contaminants using Field Portable Ultraviolet and Visible Light (UV/Vis) Spectrophotometry"**

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Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
2005		**-**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Detection Levels of Drinking Water Contaminants using Field Portable Ultraviolet and Visible Light (UV/Vis) Spectrophotometry	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Uniformed Services University of the Health Sciences,F. Edward Hebert School of Medicine,4301 Jones Bridge Road,Bethesda,MD,20814-4799**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
see report

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**		**70**	

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ABSTRACT

Title of Thesis: "Detection Levels of Drinking Water Contaminants using Field Portable Ultraviolet and Visible Light (UV/Vis) Spectrophotometry"

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The current EPA approved methods for the analysis of drinking water contaminants are expensive, require skilled lab technicians, and are not conducive to military field operations. The HACH DR/4000-U offers an easier, more portable, water detection system using a Ultraviolet/Visible Spectrophotometer. The DR/4000U was tested against 19 EPA inorganic drinking water contaminants at six concentrations.

For all 19 contaminants, the DR/4000U was able to detect well below the EPA Maximum Contaminant Levels. The DR/4000U was reasonably accurate and precise. The highest four concentrations were within 25% of the known standards for all 19 contaminants. 97% of the replicate samples analyzed at the highest four concentrations had less then 25% RSD. The system is reasonably compact and rugged but the delicate glassware, many reagents and cleanliness indicate this system is well suited to a climate controlled operating location but is not well suited to field use.

DETECTION LEVELS OF DRINKING WATER CONTAMINANTS USING FIELD PORTABLE ULTRAVIOLET AND VISIBLE LIGHT (UV/VIS) SPECTROPHOTOMETRY

BY

MAJ SCOTT H. NEWKIRK

Thesis submitted to the Faculty of the Department of Preventive Medicine and Biometrics Graduate Program of the Uniformed Services University of the Health Sciences in partial fulfillment of the requirement for the Degree of Master of Science in Public Health, 2005

DEDICATION

To my wife, Kristin and my daughter Isabelle for the sacrifices you have made during my career as an Army Officer and through the last two years of school. My accomplishments would not be possible without your never-ending support. I love you.

ACKNOWLEDGEMENT

I would like to thank the Navy Environmental Health Center and the Navy Environmental and Preventive Medicine Unit 2 for providing support and funding to complete this work. Additionally, I would like to thank Mr. Greg Most from the HACH Company for his willingness to provide his technical expertise and support with equipment needs early on in the work.

I would like to thank all the members of my committee for their tireless efforts, support, and dedication in assisting me in the completion of this study and the degree program. I want to especially thank COL Robert Lipnick and COL (Retired) Robert Fitz for their belief in me, encouragement, and their mentorship.

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Statement of the Problem

As the length of military deployments continue to increase, the need to accurately identify and quantify contaminants found in field drinking water is essential in the medical surveillance of military personnel. Currently, there are only four inorganic contaminants of military concern (Arsenic, Cyanide, Sulfate, Chloride) listed on the Department of Defense (DoD) short and long-term field water quality standards (USA, 1999). These contaminants are listed because of their acute affects on military personnel. As a result of unexplained illnesses seen after the Gulf War in the early 1990s, monitoring and reporting of occupational and environmental hazards that may cause chronic or lifetime effects is now being conducted (NSTC, 1998). There is a need in the military to have the capability to analyze water supplies for an additional 15 inorganic chemicals, mirroring the Environmental Protection Agency's (EPA) Primary and Secondary Drinking Water Standard for inorganic chemicals (USA, 1999; EPA, 2004a).

Primary Inorganic Contaminants	Secondary Inorganic Contaminants
Arsenic *	Aluminum
Barium	Chloride *
Beryllium	Copper
Cadmium	Fluoride
Copper	Iron
Cyanide *	Manganese
Fluoride	Silver
Lead	Sulfate *
Mercury	Zinc
Nitrate	
Nitrite	
Selenium	

Table 1-1. EPA's Safe Drinking Water Standards
* Required to test by deployed military units

The ultimate goal is to have military field drinking water tested and monitored for the same contaminants as any municipal water distribution system found in the United States. A challenge in meeting this goal for military preventive medicine units is finding an analysis instruments that is relatively lightweight, user-friendly, durable, without compromising the instrument's sensitivity and ability to collect reproducible data (Kimm, 2002).

One analysis method currently being used by military preventive medicine units is ultraviolet/visible light (UV/Vis) Spectrophotometry. The HACH Company's DR/4000 is a UV/Vis spectrophotometer that is being used in many military units. The DR/4000 is capable of analyzing inorganic contaminants in various water sources to include all the inorganic EPA Safe Drinking Water Standards. However, its ability to accurately analyze drinking water contaminants at relevant concentrations is not well studied and serves as the basis for this research.

Background

Both the military and the EPA require testing for inorganic contaminants in drinking water that adversely effect human health; are known or likely to occur at a frequency and level of public health concern; and because regulation of the contaminant levels presents an opportunity to reduce the health risk to persons using the water system (USA, 1999; EPA, 2004b). Chemicals on the EPA's primary drinking water standard are regulated based on the general population and a long exposure period (EPA, 2004a). Contaminants listed on the secondary drinking water standard are non-enforceable guidelines, developed to control for cosmetic effects such as skin and tooth discoloring or aesthetics of drinking water such as color, taste, odor (EPA,2004b). The military's

approach to field drinking water standards is based on acute health effects to consumers who are healthy adult service members with a short duration of exposure and larger water consumption rates (USA, 1999).

The same risk analysis techniques are used for computing EPA drinking water standards and military standards but the assumptions differ. The EPA sets maximum concentration level goals (MCLGs) for contaminants that can cause negative health effects. The MCLG is the concentration deemed safe for human consumption. The EPA then establishes a Maximum Concentration Level (MCL), which is the maximum concentration allowed in drinking water. The MCLs are enforceable standards and are set as close to the MCLGs as possible (EPA, 2004b). The military establishes its own safe drinking water standards for the four contaminants shown in Table 1-1 using a different set of assumptions (USA, 1999). However, as the length of deployments continues to grow longer or service members return for another rotation, certain assumptions may be called into question.

There are also different approaches in the analysis of drinking water between municipal drinking water laboratories and military preventive medicine units in deployed settings. The Code of Federal Regulations (EPA, 2004a), which governs the safety of public drinking water, stipulates analytical procedures that are approved for the detection of the contaminants listed on the EPA's primary and secondary drinking water standards. Eight of the twelve approved methods for the primary drinking water standard require an Atomic Absorption Spectrometry (AAS) or an Inductively Coupled Plasma (ICP) (EPA, 2004a). These methods are very sensitive, reliable, and accurate, however, they are also expensive, complicated, and time consuming for use by the military in deployed situations (Ferree, 2001).

Comment:

HACH DR/4000 UV/Vis Spectrophotometer

A UV/Vis Spectrophotometer could serve as an alternate water analysis tool for the military. UV/Vis Spectrophotometers may not be as sensitive as equipment required by EPA drinking water standards (Campbell, 1998). However, because UV/Vis Spectrophotometers are relatively inexpensive, easy to use, relatively fast and portable, it has many advantages for military use (Ferree, 2001/Vailant, 2002/Ormaza, 1994).

The DR/4000U, UV/Vis Spectrophotometer, quantifies chemicals by the degree of absorption from certain wavelengths in the near infrared, visible light, and ultra-violet light spectrum (HACH, 2003). The DR/4000U has a deuterium source lamp for UV light spectrum analysis and a gas-filled tungsten source lamp for visible light spectrum analysis. The DR/4000 is capable of automatically scanning multiple wavelengths and is capable of time course operations. Time course operations allow the instrument to measure reactions of a sample by taking readings of one wavelength over a period of time. This enables the user to determine how quickly color develops in a sample, how stable it is, and how soon it decays. The DR/4000U also has the ability to measure a sample at a maximum of four different wavelengths in rapid succession in one operation, enabling a user to determine the most efficient wavelength for a sample. The DR/4000U has an optical system composed of a light source, a split-beam monochromator and silicon photodiode detectors. The monochromator has an operating range of 190-1100-nanometers (nm) with an internal calibration upon system start-up. The DR/4000 has preprogrammed calibrations for more than 130 methods that correspond to individual contaminants and the ability to store up to 200 personal methods in its memory. Because UV/Vis technology is not an approved EPA method for drinking water, it has not been widely researched for this application. Most literature on UV/Vis

spectrophotometry has been associated with analyses of wastewater, aquaculture, agricultural and food service products.

Research Objective

Determine the sensitivity, accuracy, variability and usability of the DR/4000 UV/Vis Spectrophotometer for the analysis of the 19 inorganic contaminants listed in the EPA's Primary and Secondary Drinking Water Standards.

Specific Aims

Specific Aim 1: Quantify the calculated lower limit for 19 inorganic contaminants listed in the EPA's drinking water standards using the DR/4000 UV/Vis Spectrophotometer. Compare the calculated lower limit to the EPA MCL and the HACH Lower Limit.

Specific Aim 2: Determine the accuracy of the DR/4000 for the 19 chemicals tested with six known standards for each chemical.

Specific Aim 3: Determine the variability at each concentration with the 10 replicate samples.

Specific Aim 4: Identify the limitations, which would impact the usability of the instrument for use in a military field setting

CHAPTER TWO: LITERATURE REVIEW

Identifying, analyzing, and being able to accurately report levels of contaminants in military field drinking water stems directly from lessons learned from previous military operations. In particular, ailments of unknown origins afflicting personnel returning from the Gulf War in the 1990s, prompted Presidential Review Directive 5 (PRD-5), which provided direction to government agencies to prevent such health effects in future military operations. The directive was designed to improve the collection of health and exposure data and increase knowledge of possible health risks (NSTC, 1998). PRD-5 and other Department of Defense (DoD) Directives led to the issuance of DoD Directive 6490-2, Joint Medical Surveillance, assigning responsibility to military preventive medicine units to increase monitoring of environmental, occupational, and epidemiological threats that could impact military personnel during active Federal service, especially military deployments (DoD, 1997). Surveillance of field drinking water is an important component of the Joint Medical Surveillance Program and the military preventive medicine mission. Safe drinking water is a critical element in any successful military operation and towards the health of service members.

As previously discussed, AAS and ICP technologies are not conducive to military field operations. Currently, water samples are transported out of the military deployment area to laboratories for confirmatory testing of contaminant concentrations (HQDA, 2001). The UV/Vis Spectrophotometer may alleviate the need to send water samples to a laboratory, which is very time consuming. However, the accuracy, precision, and reliability of UV/Vis spectrophotometry has not been well studied for analyzing inorganic contaminants in drinking water at concentrations near regulatory limits.

Most water analysis using UV/Spectrophotometry has been used in the areas of wastewater (municipal and industrial), aquaculture, and agriculture (Deflandre and Gagne, 2001; Brookman, 1997; Karlsson et al., 1995). One study tested a field portable HACH DR/2000 spectrophotometer using the visible light spectrum along side a laboratory-based Shimadzu UV-2100 spectrophotometer (Shimadzu Scientific Instruments, Columbia, Maryland). Phosphate, nitrate and nitrite from aquacultural pond waters were used to compare the instruments. Nitrate and nitrite are chemicals with primary drinking water standards. To compare absorbance and detection limits, prepared samples with deionized water and standard solutions were used. The Shimadzu UV-2100 and the HACH DR/4000 spectrophotometers were found to have comparable absorbance readings with similar standard deviations as shown in Table 2-1. The portable HACH DR/2000 spectrophotometer was found to have higher detection limits than that of the laboratory-based Shimadzu instrument. The authors concluded that the HACH DR/2000 provides adequate sensitivity for monitoring water quality in aquacultural systems. (Ormaza-Gonzbl and Illalba-Flor, 1994).

		ppm	HACH DR/2000	Shimadzu UV-2100
Absorbance:				
	Nitrite	1	0.066 ± 0.001	0.065 ± 0.012
	Nitrate	0.3	0.029 ± 0.001	0.034 ± 0.002
	Phosphate	0.3	0.040 ± 0.002	0.037 ± 0.004
Detection Limits:				
	Nitrite		0.3 ppm	0.048 ppm
	Nitrate		0.657 ppm	0.049 ppm
	Phosphate		0.162 ppm	0.05 ppm

Table 2-1 Comparative data for HACH 2000 and Shimadzu UV-21000

Studies using UV/Vis spectrophotometry for the analysis of wastewater show reliable results typically found in wastewater sources (Ferree, 2001, Balasubramanian and Pugalenthi, 1999, Thomas, et al., 1997). In a study comparing the recovery of total chromium from tannary wastewater a Jobin Yvon JY-24 ICP-Atomic Emission Spectrometry (AES) (Horiba Jobin Yvon Inc, Edison, New Jersey), a Perkin-Elmer AAS-3010 Flame AAS (Perkin Elmer, Wellesley, Massachusetts), and a double-beam Shimadzu UV/Vis spectrophotometer were evaluated. Three samples from five different categories of tannery waste were analyzed by all three analytical methods for total chromium resulting in recovery rates of 99-100% by the UV/Vis method and a rate of 95-98% by the ICP-AES and FAAS methods. The authors believe that interferences caused by a high acid content coupled with high concentrations of electrolytes weighed heavily on the ICP and FAAS techniques' ability to recover total chromium from the samples. The UV/Vis spectrophotometric method was found to be a more suitable method when compared to the other two analytical methods for this application.

In a separate comparison study utilizing UV/Vis technology, a Perkin-Elmer Lambda-4-40 UV/Vis spectrophotometer was tested against ion chromatography, a common technique used in the analysis of nitrate, to assess the UV/Vis method's ability to recover nitrate from 27 wastewater samples and nitrogen from 52 wastewater samples. An analysis by linear regression revealed a strong relationship between the two methods resulting in a coefficient of determination or $r^2 = 0.99$ for both contaminant analysis. This UV/Vis method proved to be accurate after comparison with quality control samples using known concentrations, resulting in a recovery difference of 0.2% for nitrate and 0.4% for nitrogen from the certified standard. The authors make note that the UV/Vis

method also proved to be a fast, simple technique for both nitrate and total nitrogen, without compromising accuracy and precision (Ferree and Shannon, 2001).

UV/Vis spectrophotometry has proven to be an efficient and reliable method in the determination of water quality parameters of wastewater operations, agriculture and the aquaculture industries. Some limitations have been identified with the simplified chemistry associated with the UV/Vis methods (Ormaza and Illalba, 1994). The absorbance from competing pollutants, such as sugars in food industry effluents, or oil and grease found in wastewater samples can cause erroneous readings (Vallient and Thomas, 2002). However, accuracy, precision, and other performance measures were found to be comparable with approved methods for respective analytes (Ferree and Shannon, 2001, Ormaza and Illalba, 1994, Chevalier et al., 2002). These findings offer some basis to believe that UV/Vis spectrophotometry can provide reliable results in the analysis of field drinking water. However, accurately detecting contaminants at the regulatory limits of the EPA's primary and secondary drinking water standards could prove more difficult than analyzing water sources associated with wastewater, agriculture, and aquacultural operations.

CHAPTER THREE: METHODS

In order to test the accuracy, variability and sensitivity of the HACH DR/4000U instrument against the 19 inorganic EPA drinking water standards, six concentrations were selected for each chemical. The HACH Company typically advertises a detection range for each analysis method to be from zero to the estimated Upper Limit (UL) of detection. Arsenic, for example, is advertised to detect from 0 to 0.200 mg/L. The six concentrations for each chemical were determined based on the following percentages of the chemicals' UL of detection: 90^{th}, 50^{th}, 25^{th}, 10^{th}, 5^{th}, and 1^{st} percentile. So arsenic, with an HACH UL of detection of 0.200 mg/L, was tested at the concentrations of 0.180, 0.100, 0.050, 0.020, 0.010, 0.002 mg/L. Test levels for contaminants on the primary and secondary drinking water standards are listed in Table 3-1.

	Contaminant	UL of Detection (mg/L)	Percentile Concentration of the HACH UL of Detection (UL) - mg/L					
			90th	50th	25th	10th	5th	1st
Primary	Arsenic	0.20	0.18	0.10	0.05	0.02	0.01	0.00
	Barium	100.00	90.00	50.00	25.00	10.00	5.00	1.00
	Cadmium*	80.00	72.00	40.00	20.00	8.00	4.00	0.80
	Chromium	0.70	0.63	0.35	0.18	0.07	0.04	0.01
	Copper	1.3**	1.17	0.65	0.33	0.13	0.07	0.01
	Cyanide	0.24	0.22	0.12	0.06	0.02	0.01	0.00
	Fluoride	2.00	1.80	1.00	0.50	0.20	0.10	0.02
	Lead*	150.00	135.00	75.00	38.00	15.00	8.00	2.00
	Mercury*	2.50	2.25	1.25	0.63	0.25	0.13	0.03
	Nitrate	5.00	4.00	2.50	1.25	0.50	0.25	0.05
	Nitrite	0.30	0.27	0.15	0.08	0.03	0.02	0.00
	Selenium	1.00	0.90	0.50	0.25	0.10	0.05	0.01
Secondary	Aluminum	0.25	0.23	0.13	0.06	0.03	0.01	0.00
	Chloride	25.00	22.50	12.50	6.25	2.50	1.25	0.25
	Iron	1.80	1.62	0.90	0.45	0.18	0.09	0.02
	Manganese	0.70	0.63	0.35	0.18	0.07	0.04	0.01
	Silver	0.70	0.63	0.35	0.18	0.07	0.04	0.01
	Sulfate	70.00	63.00	35.00	17.50	7.00	3.50	0.70
	Zinc	3.00	2.70	1.50	0.75	0.30	0.15	0.03

* ug/L

** Contaminant tested against EPA MCL rather than UL of Detection

Table 3-1. Test levels for contaminants listed on EPA primary and secondary standard

Determination of Calculated Lower Limit

The calculated lower limit or otherwise known as the Method Detection Level (MDL) is the lowest limit that the instrument can detect after going through the entire sample preparation process prior to analysis. The HACH Company does not provide lower limit values for their instruments, but instead provide an estimate of the lower limit called the Estimated Detection Level (EDL). For the purposed of this study, the MDL will be called the Calculated Lower Limit and the HACH EDL will be called the HACH Lower Limit.

The calculated lower limits for the DR/4000 were determined for each chemical listed on the EPA's primary and secondary drinking water standard. The calculated lower limits were based on the manufacture's directions for determining a lower limit using the instrument (HACH, 2003). For each contaminant, ten replicate samples (at least seven is recommended by HACH) at a concentration of 3 times the HACH lower limit (HACH recommends 2-3 times the HACH lower limit), were analyzed to produce a mean and standard deviation. The calculated lower limit was determined by multiplying the standard deviation by the appropriate t-value for a 99% upper confidence limit.

If a HACH lower limit was not provided for a chemical or no test percentile of the UL of detection was approximate to 3 times the HACH lower limit (a condition set by the manufacturer in determining a calculated lower limit), the following steps were followed to determine the chemical's calculated lower limit. Temporary calcultated lower limits were determined using concentrations at the 1^{st} and 5^{th} percentiles of the UL of detection. The average value from the two temporary calculated lower limits was used as the final calculated lower limit for the chemical. Based on observations of the 16 chemicals that the manufacturer provided estimated lower limits for, the concentration equal to 3 times

the HACH lower limit occurred primarily at the 1st and 5th percentiles. Therefore, the mean value of the 1st and 5th percentiles was used as a starting point in the determination of the calculated lower limits.

GENERAL ANALYSIS TECHNIQUES

To ensure complete accuracy of volumes used during analytical procedures, all measured solutions were weighed using a Denver Instruments, 0-200 gram (g), Apex Series Balance calibrated in accordance with reference standards traceable to the Institute of Standards and Technology with a certificate of calibration dated 14 October 2004.

Three sets of precision-matched glass sample cells, which hold a maximum of 25mL, were used during all analytical procedures. Precision-matched sample cells have been grouped together in a set of two or in sets of eight by the manufacturer. During the production of each lot of sample cells, the manufacturer tests the absorbance and transmittance through each cell and then groups cells with matched rates of absorbance and transmittance together forming a set of precision-matched cells. The sets used in this study were numbered 118, 227, and 224 (HACH, 2005).

ANALYTICAL PROCEDURES

All samples were mixed using deionized water produced by a Millipore® Solution 2000, Water Purification System, with a range of 18.34 – 18.58 resistivity. All chemical standard solutions and reagents used in the analytical procedures were obtained directly from the HACH Company. All analytical methods used to obtain contaminant MDLs were provided by the HACH Company's analytical procedures for the DR/4000 UV/Vis spectrophotometer. Ten replicate samples at six known concentrations based on a

percentage of the EDL were performed for each chemical. The analytical procedure for each of the 19 chemicals tested will be detailed in the rest of this chapter.

Arsenic

The HACH procedure 0001, Silver Dietrhyldithiocarbamate Method for Arsenic was used. The wavelength was 520 nanometers (nm) for this method. In a fume hood, the HACH distillation apparatus for arsenic recovery was assembled (Figure 3-1).

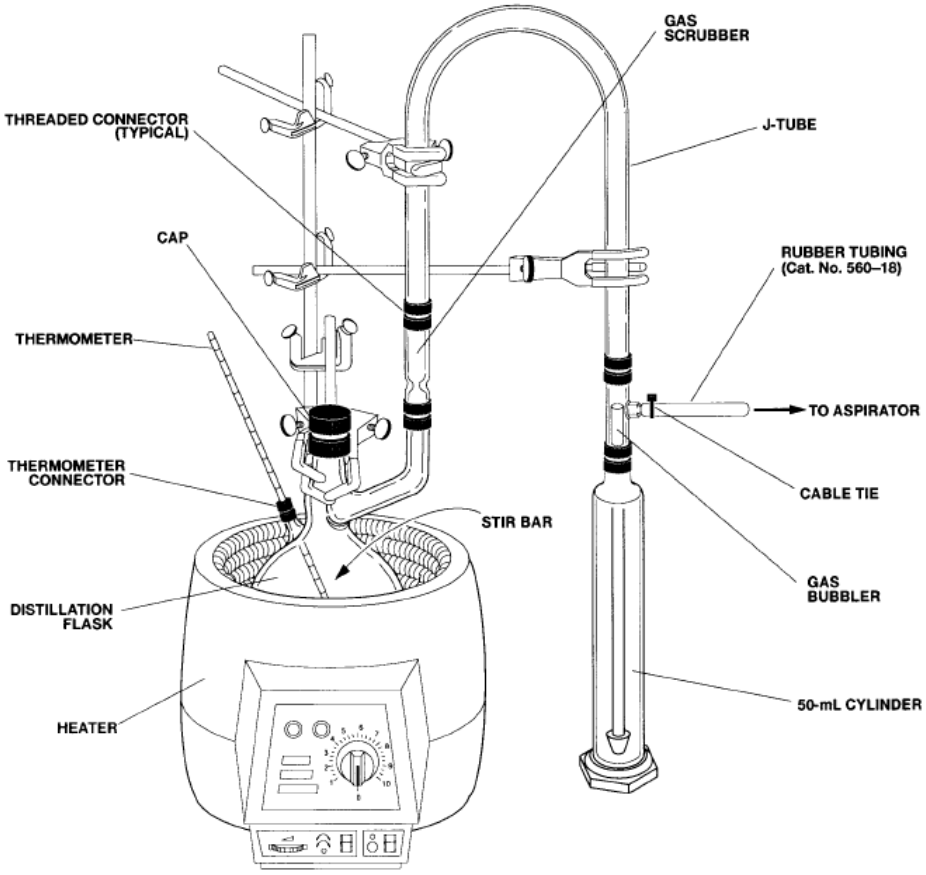

Figure 3-1. Arsenic Distillation Assembly

1. Place a cotton ball dampened with a 10% lead acetate solution in the glass gas scrubber.
2. Add 25 mL of arsenic absorber solution the 50 mL cylinder below the gas scrubber
3. Add 250 mL of water sample to distillation flask.
4. Add 25 mL of hydrochloric acid, 1 mL of stannous chloride, 3 mL of potassium iodide to distillation flask.
5. Cap distillation flask and do not disturb for a 15 minute period.
6. Add 6g of zinc to the distillation flask and cap immediately.
7. Heat distillation flask at a medium heat setting for 15 minutes.
8. Reduce to lowest heat setting and heat for another 15 minutes.
9. 25 mL of arsenic absorber solution was placed into a sample cell and placed into the DR/4000 as a sample blank.
10. The sample blank was removed and the 25 mL of the reacted sample was transferred to a matched cell and placed into the DR/4000 for analysis.

Barium

The HACH procedure 1100, Turbidimetric Method for Barium was used. The wavelength was 450 nm for this method.

1. Fill a clean, dry sample cell with 25 mL of the prepared sample.
2. Add contents of one BariVer 4 Barium Reagent Powder Pillow and swirl to mix.
3. Allow samples to be undisturbed during a 5 minute reaction period.
4. Fill a second sample cell (sample blank) with 25 mL of the prepared sample

5. After the 5 minute reaction period, the second sample cell was placed in the DR/4000 as the sample blank.
6. The sample blank was removed from the DR/4000 and the sample cell with 25 mL of reacted sample was inserted for analysis.

Cadmium

The HACH procedure 8017, Dithizone Method for Cadmium was used. The wavelength was 515 nm for this method.

1. 250 mL of sample was added to a 500mL separatory funnel.
2. Add content of one Buffer Powder Pillow for heavy metals, citrate type.
3. Cap funnel and shake to dissolve reagent powder in the sample.
4. Add 30 mL of chloroform and one DithiVer Metals Reagent Powder Pillow.
5. Cap funnel and invert several times to mix the solutions and powdered reagent.
6. Add 20 mL of 50% sodium hydroxide solution and a 0.1 gram (g) scoop of potassium cyanide to the funnel.
7. Shake the funnel vigorously for 15 seconds and then remove stopper and leave undisturbed for one minute.
8. Add 30 mL of DithiVer solution to the separatory funnel, stopper funnel, then shake. Allow to vent by removing the stopper and then shake and vent twice more.
9. Stopper funnel and the shake funnel vigorously for one minute.
10. Allow funnel to remain undisturbed for five minutes.
11. Insert a cotton plug into the separatory funnel's delivery tube
12. Slowly drain 25 mL of sample into a clean sample cell.

13. Fill a second sample cell with 25 mL of chloroform (sample blank).
14. The sample cell containing the 25 mL of chloroform was placed in the instrument as the sample blank.
15. The sample blank was removed from the DR/4000 and the sample cell with 25 mL of reacted sample was inserted for analysis.

Cadmium Unicell Method

The HACH procedure 5011, Cadion Method for Cadmium was used. The wavelength was 552 nm for this method.

1. Add 10 mL of sample into reaction tube.
2. Add 1 mL of Complexing Agent A (HCT 154 A) to the reaction tube, close the lid, and invert several times to mix.
3. Add 0.5 mL of Stabilizer Solution B (HCT 154 B) into a sample vial (light red cap), close lid and invert several times to mix.
4. The pretreated sample vial was placed into the DR/4000 as the sample blank.
5. Add 5 mL of sample from the reaction tube into the same sample vial.
6. Allow sample vial to remain undisturbed for 30 seconds.
7. The sample vial was inserted for analysis.

Chromium

The HACH procedure 1580, Alkaline Hypobromite Oxidation Method for Total Chromium was used. The wavelength was 540 nanometers (nm) for this method.

1. Fill two sample cells with 25 mL of the prepared sample (One sample cell serves as the blank)

2. Add the contents of one Chromium 1 Reagent Powder Pillow to the sample cell and then swirl to mix.
3. Place sample cell into a boiling water bath for a 5 minute period.
4. Remove from boiling water bath and place in a cooling bath until the sample reaches 25 °C.
5. Add the contents of one Chromium 2 Reagent Powder Pillow to the sample cell and then swirl to mix.
6. Add the contents of one Acid Reagent Powder Pillow to the sample cell and then swirl to mix.
7. Add the contents of one ChromaVer 3 Chromium Reagent Powder Pillow to the cell and swirl to mix.
8. Allow sample to remain undisturbed for a 5 minute reaction period.
9. The untreated sample cell was placed into the DR/4000 as the sample blank.
10. The sample blank was removed from the DR/4000 and the sample cell with 25 mL of treated sample was inserted for analysis.

Copper

The HACH procedure 1700, Bicinchoninate Method for Copper was used. The wavelength was 560 nm for this method.

1. Fill two sample cells with 10 mL of the prepared sample (one serves a sample blank).
2. Add the contents of one CuVer 1 Copper Reagent Powder Pillow to one cell and swirl to mix (prepared sample).
3. Allow prepared sample to remain undisturbed for a 2 minute period.

4. After the 2 minute reaction period, the untreated sample cell was placed in the DR/4000 as the sample blank.
5. The sample blank was removed from the DR/4000 and the sample cell with 10 mL of reacted sample was inserted for analysis.

Cyanide

The HACH procedure 1750, Pyridine-Pyrazalone Method for Cyanide was used. The wavelength was 612 nm for this method.

1. Fill two sample cells with 10 mL of the prepared sample (the first sample cell served as the blank for the procedure).
2. Add the contents of one CyaniVer 3 Cyanide Reagent Powder Pillow to the second of the two sample cells, stopper and then shake for 30 seconds to mix.
3. Allow sample to remain undisturbed for an additional 30 second reaction period.
4. Add the contents of one CyaniVer 4 Cyanide Reagent Powder Pillow, cap, and shake for 10 seconds.
5. Immediately following the 10 seconds of shaking, add the contents of one CyaniVer 5 Cyanide Reagent Powder Pillow, stopper and shake vigorously to mix the reagents.
6. Leave sample cell undisturbed for 30 minutes.
7. After 30 minute period, the untreated sample cell was placed in the DR/4000 as the sample blank.
8. The sample blank was removed from the DR/4000 and the sample cell with 10 mL of reacted sample was inserted for analysis.

Fluoride

The HACH procedure 1900, SPADNS Method for Fluoride was used. The wavelength was 580 nm for this method.

1. Fill a sample cell with 10 mL of the prepared sample.
2. Fill a sample cell with 10 mL of deionized water (sample blank).
3. Add 2.0 mL of SPADNS Reagent to prepared sample, swirl to mix.
4. Allow sample cell to remain undisturbed for a 1 minute period.
5. After the 1 minute reaction period, the sample cell containing deionized water was placed in the DR/4000 as the sample blank.
6. The sample blank was removed from the DR/4000 and the sample cell with 10 mL of reacted sample was inserted for analysis.

Lead

The HACH procedure 2210, LeadTrak Fast Column Extraction Method for Lead was used. The wavelength was 477 nm for this method.

1. Fill a 100 mL plastic graduated cylinder with 100 mL of the prepared sample and pour into a plastic beaker.
2. Add 1.0 mL of pPB-1 Acid Preservative Solution to the beaker and leave undisturbed for a 2 minute period.
3. Add 2.0 mL of pPb-2 Fixer Solution to the beaker and swirl to mix.
4. Slowly pour the entire content of the beaker into the Fast Column Extractor (Figure 3-2).

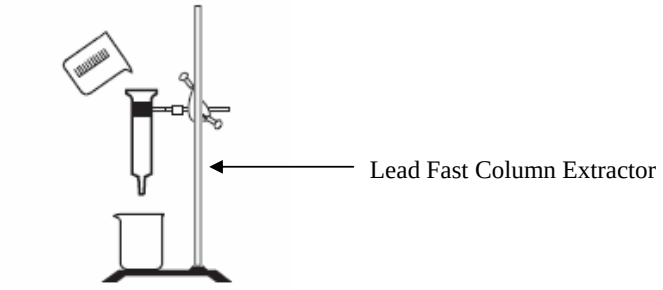

Figure 3-2. Lead Fast Column Extractor

5. Place a 150 mL beaker under the Fast Column Extractor to capture the solution as it flowed through the Extractor.
6. Once the flow has stopped, fully compress the absorbent pad in the Extractor using the accompanying plunger.
7. Place a clean sample cell under the Extractor and pipette 25 mL of pPb-3 Eluant Solution into the Extractor.
8. After the Eluant Solution starts to drip from the Extractor, force the remaining Eluant Solution out by inserting the plunger, ultimately discharging 25 mL of solution into the sample cell.
9. Add 1.0 mL of pPb-4 Neutralizer Solution to the sample cell, then swirl to mix.
10. Immediately add the contents of one pPb-5 Indicator Powder Pillow to the sample and swirl to fully mix the powder and solution.
11. Allow sample to remain undisturbed for a 2 minute period.
12. Following the reaction period, place the sample cell in the DR/4000 as the sample blank.

13. After a reading of –2ug/L Pb (the program uses a non-zero y-intercept), remove the sample cell and add 6 drops of pPb-6 Decolorizer Solution and swirl to mix.
14. The sample cell with 25mL of reacted sample was inserted into the DR/4000 for analysis.

Mercury

The HACH procedure 2270, Cold Vapor Mercury Preconcentration Method for Mercury was used. The wavelength was 412 nm for this method.

1. Add one liter of sample to a 2000 mL Erlenmeyer flask along with a 50 millimeter magnetic stir bar.
2. Place flask on a magnetic stir plate.
3. While the sample is stirring, add 50 mL of concentrated sulfuric acid followed by 25 mL of nitric acid.
4. Add 4.0 g of potassium persulfate to the sample and allow to stir until dissolved.
5. Add 7.5g of potassium permanganate to the sample and allow to stir until dissolved.
6. Add 0.5g spoonfuls of hydroxylamine-hydrochloride in 30 second increments until the sample was clear and all the manganese dioxide is dissolved.
7. Remove magnetic stir bar transfer the contents of the flask into a cold-vapor washing bottle.
8. Connect a mercury absorber column to the washing bottle, followed by connecting a 100 mL Erlenmeyer flask to the mercury absorber column.

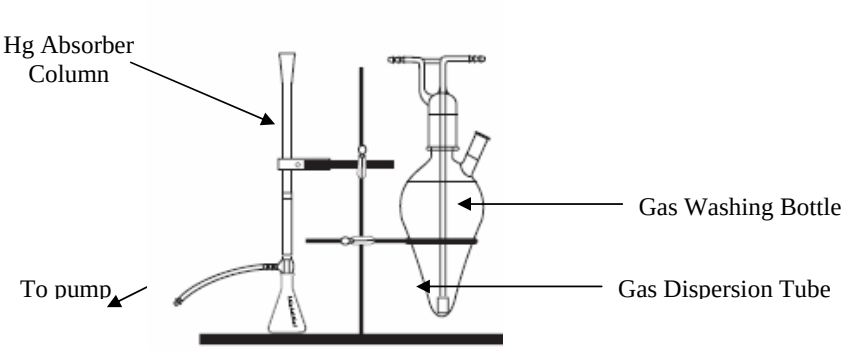

Figure 3-3. Cold Vapor Mercury Apparatus

9. Add 8 mL of HgEx Reagent B into the mercury absorber column.
10. Connect the mercury absorber column to an electric vacuum pump to draw out most of the HgEx B solution into the 100 mL Erlenmeyer flask.
11. Disconnect pump using quick disconnect once most of the solution has been drawn from the mercury absorber column
12. Remove the flask and replace with a 10 mL distilling receiver.
13. Add 2 mL of HgEx Reagent C into the mercury absorber column.
14. Connect the column to the gas washing bottle using a glass elbow and plastic tubing.
15. Add the content of one ampule of HgEx Reagent A through the gas washing bottle's side neck to suspend any undissolved reagents, then stopper.
16. Reconnect the vacuum pump to the mercury absorber column using the quick disconnect.
17. Pull the HgEx Reagent C through the mercury absorber column and into the 10 mL distilling receiver.

18. Start a 5 minute reaction period to allow gas bubbles to disperse from the gas dispersion tube in the gas washing bottle and for the mercury to be captured by the mercury absorber column.
19. After the 5 minute period, with the vacuum pump still connected, add 8 mL of HgEx Reagent B to the mercury absorber column to elute the captured mercury, pulling the Reagent B solution into the distilling receiver.
20. Fill the distilling receiver with 10 mL of the sample and turn off the vacuum pump.
21. Remove the distilling receiver from the mercury column and replace with the 100 mL Erlenmeyer flask.
22. Add 3 mL of HgEx Reagent B to the column to keep the absorber packing wet between tests.
23. Add the contents of one HgEx Reagent 3 foil pillow to the 10 mL distilling receiver, stopper, and invert to dissolve reagent thoroughly.
24. Add contents of one HgEx Reagent 4 to the distilling receiver, stopper, and invert to dissolve the reagent.
25. Add 8 drops of HgEx Reagent 5 to the distilling receiver, stopper and inverted to mix solutions.
26. Transfer solution into a sample cell and allowed to be undisturbed for a 2 minute reaction period.
27. After the 2 minute period, the sample cell was placed into the DR/4000 as the sample blank.
28. Remove sample cell from the instrument and add the contents of one HgEx Reagent 6 foil pillow to the sample cell and swirl to mix.

29. Return the sample cell to the instrument for analysis of the sample.

Nitrate

The HACH procedure 2520, Cadmium Reduction Method for Nitrate was used. The wavelength was 400 nm for this method.

1. Fill two sample cells 10 mL of the prepared sample (One serves as sample blank).
2. Add the contents of one NitraVer5 Nitrate Powder Pillow to the initial sample cell, stopper sample cell and shake vigorously for one minute.
3. Leave sample cell undisturbed for a 5 minute period.
4. The untreated sample cell was placed in the DR/4000 as the sample blank.
5. The sample blank was removed from the DR/4000 and the sample cell with 10 mL of reacted sample was inserted for analysis.

Nitrate Unicell Method

The HACH procedure 3032, Nitrate Unicell Method for Nitrate was used. The wavelength was 370 nm for this method.

1. Add 0.2 mL of dimethylphenol solution (HCT 106A) to sample vial, cap and invert to mix.
2. Immediately remove cap and add 1 mL of sample to the vial, cap and invert to mix.
3. Leave vial undisturbed for a 15 minute period.
4. The zero vial was placed in the DR/4000 as the sample blank.
5. After the 15 minute period, the treated vial was placed in the DR/4000 for analysis of the sample.

Nitrite

The HACH procedure 2610, Diazotization Method for Nitrite was used. The wavelength was 507 nm for this method.

1. Fill two sample cells 10 mL of the prepared sample (one serves as sample blank).
2. Add the contents of one NitraVer3 Nitrite Powder Pillow to sample cell, stopper and shake to dissolve powder.
3. Leave sample cell undisturbed for a 20 minute period
4. After the 20 minute reaction period, the untreated sample cell was placed in the DR/4000 as the sample blank.
5. The sample blank was removed from the DR/4000 and the sample cell with 10 mL of reacted sample was inserted for analysis.

Selenium

The HACH procedure 3300, Diaminobenzidine Method for Selenium was used. The wavelength was 420 nm for this method.

1. Add 100 mL of deionized water into a 500 mL Erlenmeyer flask to serve as the sample blank.
2. Fill a second 500 mL Erlenmeyer flask with 100mL of the prepared sample.
3. Add a 0.2 g scoop of TitraVer Hardness Reagent to each flask and then swirl to mix.
4. Add a 0.05 g scoop of diaminobenzidine tetrahydrochloride to each flask and swirl to mix.
5. Add 5.0 mL of Buffer Solution, sulfate type, to each flask, then swirl to mix.
6. Place each flask on a hot plate until contents are brought to a gentle boil.

7. Once a gentle boil begins, begin a 5 minute reaction period.
8. After the 5 minute period, remove the flasks from the hot plates and bring to room temperature using a water bath.
9. In a fume hood, transfer the contents of each flask into two different 250 mL separatory funnels.
10. Add 2.0 mL of 12N Potassium Hydroxide Standard Solution to each funnel, stopper and shake to mix solutions.
11. Add 30 mL of toluene to each funnel, stopper, swirl and invert funnel to allow for complete mixture of the solutions, and then vent into the fume hood.
12. Invert and vent each funnel twice.
13. After venting, vigorously shake each funnel for a 30 second period and then leave undisturbed for a 4 minute period.
14. After the 4 minute reaction period, drain and discard the bottom water layer of each funnel.
15. Insert a cotton plug into each funnel's delivery tube and then slowly drain 25 mL of the sample into two separate sample cells.
16. The sample cell containing the treated deionized water was placed into the DR/4000 as the sample blank.
17. The sample blank was removed from the DR/4000 and the sample cell with 25 mL of reacted sample was inserted for analysis.

Aluminum

The HACH procedure 1010, Eriochrome Cyanide R Method for Aluminum was used. The wavelength was 535 nm for this method.

1. Rinse a 25 mL graduated mixing cylinder with 1:1 hydrochloric acid and DI water before use to avoid errors due to contaminants being absorbed on the glass surface.
2. Fill the 25 mL mixing cylinder with 20 mL of the prepared sample.
3. Add one ECR reagent powder pillow to the sample, stopper and invert several times to dissolve the reagent powder.
4. Add the contents of one Hexamethlylenetetramine Buffer Reagent Powder Pillow for a 20 mL sample to the solution, stopper, and invert repeatedly until the reagent powder was thoroughly dissolved.
5. Add one drop of ECR Masking Reagent Solution to a clean sample cell followed by 10 mL of the mixture to create the sample blank for the procedure.
6. Add the remaining 10 mL of the mixture into a second sample cell.
7. Allow the two sample cells to remain undisturbed for a 5 minute period.
8. After the 5 minute reaction period, the sample cell treated with the ECR Masking Reagent was placed into the DR/4000 as the sample blank.
9. The sample blank was removed from the DR/4000 and the sample cell with 10 mL of reacted sample was inserted for analysis.

Chloride

The HACH procedure 1400, Mercuric Thiocyanate Method for Chloride was used. The wavelength was 455 nm for this method.

1. Fill a sample cell with 25 mL of the prepared sample.
2. Fill a second sample cell with 25 mL of deionized water (sample blank).
3. Add 2.0 mL of Mercuric Thiocyanate Solution to the sample cell and swirl to mix.

4. Add 1.0 mL of Ferric Ion Solution to the sample cell and swirl to mix.
5. Leave sample cell undisturbed for a 2 minute period.
6. After the 2 minute reaction period, the sample cell with deionized water was placed into the DR/4000 as the sample blank.
7. The sample blank was removed from the DR/4000 and the sample cell with 25 mL of reacted sample was inserted for analysis.

Iron

The HACH procedure 2160, FerroMo Method for Iron was used. The wavelength was 590 nm for this method.

1. Fill a 50 mL graduated mixing cylinder with 50 mL of the prepared sample.
2. Add one FerroMo Iron Reagent 1 Powder Pillow to the sample, stopper and invert cylinder several times to dissolve the reagent powder in the sample.
3. Add 25 mL of the mixture into a sample cell.
4. Add the contents of one FerroMo Iron Reagent 2 powder pillow to the sample cell, swirl to thoroughly mix the powder.
5. Allow the sample cell to remain undisturbed for a 3 minute period.
6. Fill a second sample cell with the remaining 25 mL of the original mixture (sample blank).
7. After the 3 minute reaction period, the sample cell containing 25 mL of untreated sample was placed into the DR/4000 as the sample blank.
8. The sample blank was removed from the DR/4000 and the sample cell with 25mL of reacted sample was inserted for analysis.

Manganese

The HACH procedure 2260, PAN Method for Manganese was used. The wavelength was 560 nm for this method.

1. Fill a sample cells with 10 mL of the prepared sample.
2. Fill a second sample cell 10 mL of deionized water (sample blank)
3. Add the contents of 1 Ascorbic Acid Powder Pillow to the sample cell and swirl to dissolve the powder.
4. Add 15 drops of Alkaline-Cyanide Reagent Solution to the cell and swirl to mix.
5. Add 21 drops of PAN Indicator Solution to sample cell and swirl to mix.
6. Let sample cell remain undisturbed for a 2 minute period.
7. After the 2 minute reaction period, the sample cell with deionized was placed into the DR/4000 as the sample blank.
8. The sample blank was removed from the DR/4000 and the sample cell with 10 mL of reacted sample was inserted for analysis.

Silver

The HACH procedure 3400, Colorimetric Method for silver was used. The wavelength was 560 nm for this method.

1. Add the content of one Silver 1 Powder Pillow to a dry, 50 mL graduated mixing cylinder.
2. Add a Silver 2 Solution Pillow to the mixing cylinder and swirl to completely wet the powder.
3. Add 50 mL of the prepared sample to the graduated mixing cylinder, stopper, and invert repeatedly for one minute to thoroughly mix the sample and reagents.

4. Add 10 mL of the solution into a clean sample cell to serve as the sample blank.
5. Add the contents of one Sodium Thiosulfate Powder Pillow to sample blank and swirl to mix the powder. Leave undisturbed for a 2 minute period.
6. During the 2 minute reaction period, add 10 mL of the solution from the mixing cylinder into a sample cells.
7. After the 2 minute reaction period, the sample cell containing the untreated sample was placed into the DR/4000 as the sample blank.
8. The sample blank was removed from the DR/4000 and the sample cell with 10 mL of reacted sample was inserted for analysis.

Sulfate

The HACH procedure 3450, SulfaVer4 Method for Sulfate was used. The wavelength was 450 nm for this method.

1. Fill a clean sample cell with 25 mL of the prepared sample.
2. Add one SulfaVer 4 Reagent Powder Pillow to the sample cell and swirl to mix.
3. Allow sample cell to remain undisturbed for a 5 minute period.
4. Fill a second sample cell with 25 mL of the prepared sample to serve as the sample blank.
5. After the 5 minute reaction period, the sample cell containing the untreated sample was placed into the DR/4000 as the sample blank.
6. The sample blank was removed from the DR/4000 and the sample cell with 25 mL of reacted sample was inserted for analysis.

Zinc

The HACH procedure 3850, Zincon Method for Zinc was used. The wavelength was 620 nm for this method.

1. Rinse a 25 mL graduated mixing cylinder with 1:1 hydrochloric acid and DI water before use to avoid errors due to contaminants being absorbed on the glass surface.
2. Fill the 25 mL mixing cylinder with 20 mL of the prepared sample.
3. Add one ZincVer 5 Reagent Powder Pillow to the sample, stopper, and invert several times to mix reagent powder
4. Add 10 mL from the mixing cylinder into a clean sample cell to serve as the sample blank.
5. Add 0.5 mL of cyclohexanone to the remaining solution in the graduated mixing cylinder, stopper and shake vigorously for 30 seconds.
6. During a 3 minute reaction period, pour the contents of the mixing cylinder into a second sample cell.
7. After the 3 minute reaction period, the untreated sample cell was placed into the DR/4000 as the sample blank.
8. The sample blank was removed from the DR/4000 and the sample cell with 10 mL of reacted sample was inserted for analysis.

CHAPTER 4

RESULTS

Calculated Lower Limits

Figure 4-1 and 4-2 illustrate the calculated lower limits for the 19 chemicals listed on the EPA's primary and secondary drinking water standards. The calculated lower limit values can also be found in a table in Appendix A. The black bar in the Figure 4-1 and 4-2 illustrate the EPA MCLs. All of the EPA MCLs are much greater than the HACH lower limits and the calculated lower limits. The calculated lower limit is often a little higher than the HACH lower limit.

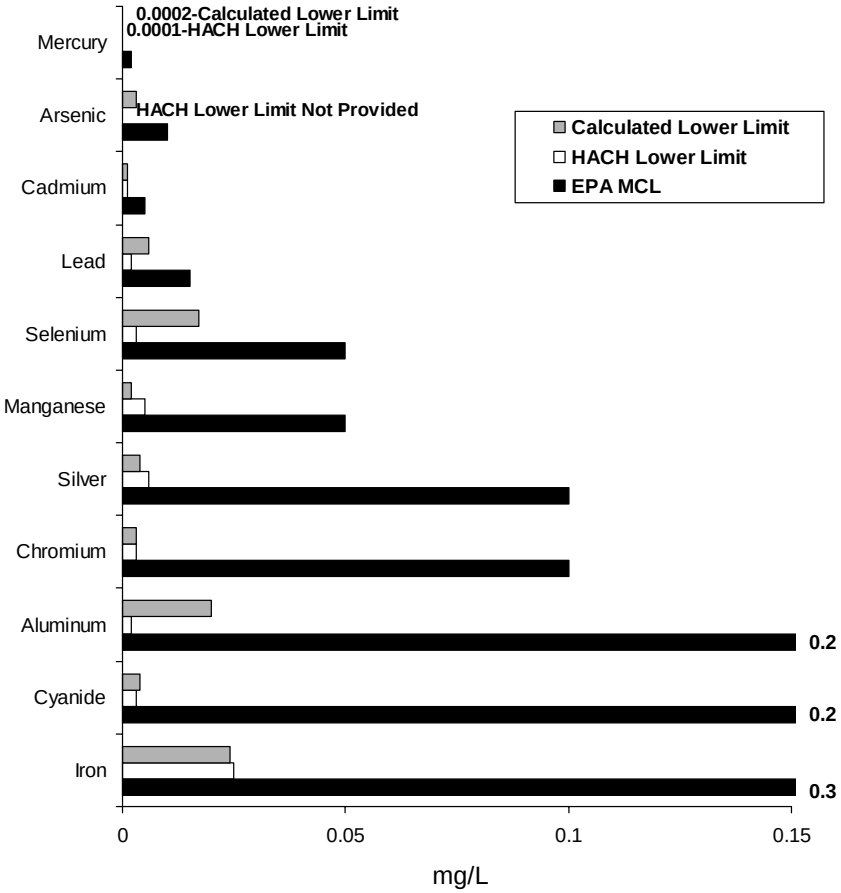

Figure 4-1. Comparison of Calculated Lower Limit/ HACH Lower Limit/ EPA MCL

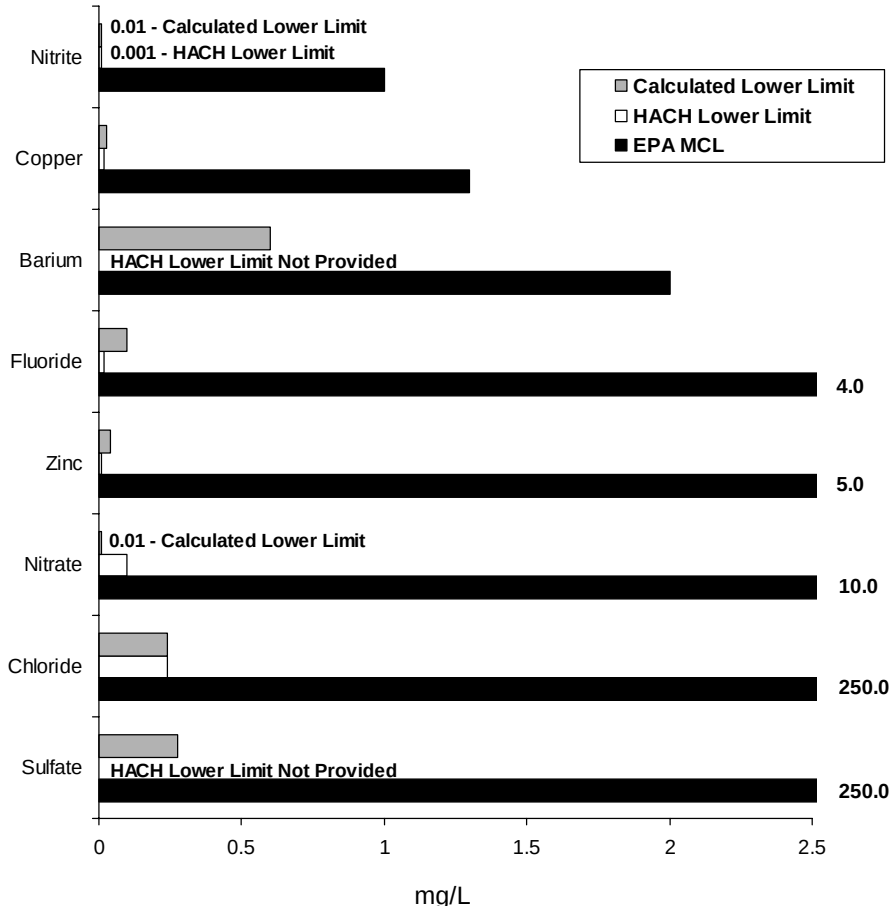

Figure 4-2. Comparison of Calculated Lower Limit / HACH Lower Limit/ EPA MCL

Determination of Accuracy

To quantify the accuracy of the instrument, results from analysis of contaminants at each concentration level were entered into the SPSS statistical software to obtain the sample mean, standard deviation, 95% confidence interval, and range. In Figure 4-3, the percent deviation is calculated by Equation 1.

$$\% \text{ Deviation} = \frac{\text{Sample Mean} - \text{Known Conentration}}{\text{Known Conentration}} * 100\% \qquad \text{Equation 1}$$

Appendix B provides this data in tabular form and appendix C illustrated the confidence interval with the known concentrations for all 19 chemicals.

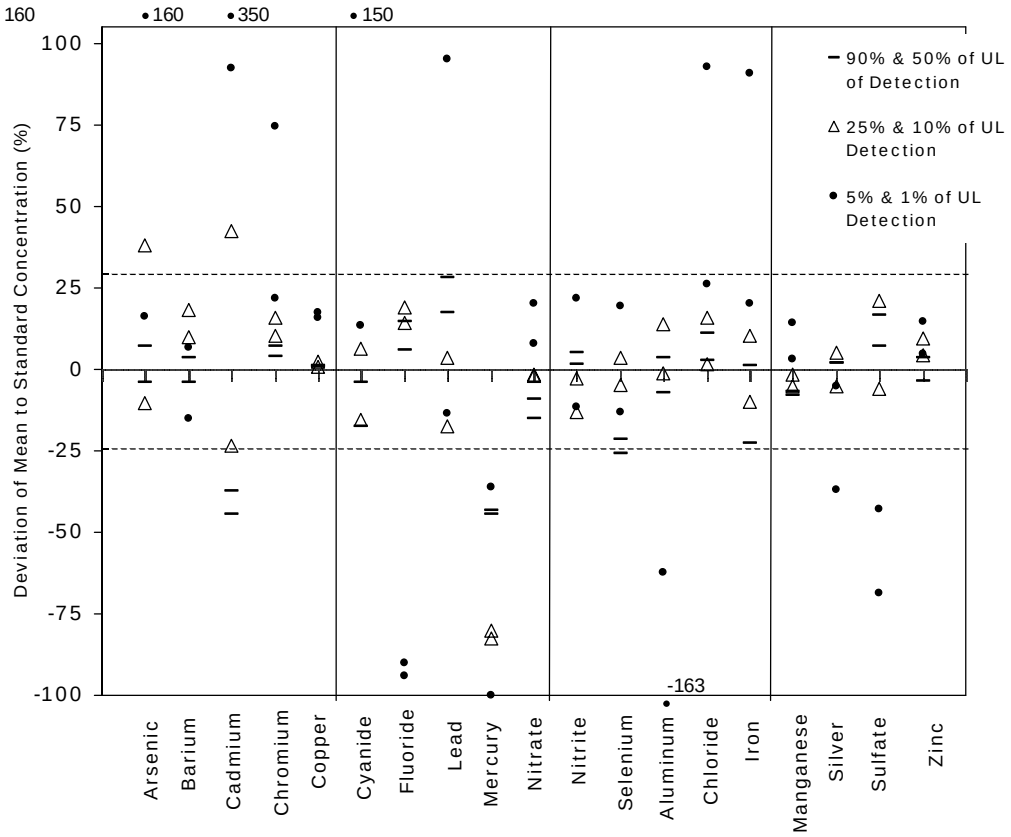

Figure 4-3. Percent Deviation of Mean to Standard Concentration

After calculating the percent deviation of the sample means at each of the highest concentrations (10, 25, 50 and 90th percentile of HACH lower limit), the data showed that 87% (66 of 76) of the percentile levels analyzed had a mean within 25% of the known concentration and 58% (44 of 76) were within 10% of the known concentration. The

most deviation from the known concentration occurred at the 2 lowest concentrations (1 and 5th percentile of HACH lower limit) with only 48% (18 of 38) of the means within 25% of the known concentration and 16% (6 of 38) within 10%.

During the analysis of mercury and nitrate, the concentration measured at the 1st percentile was found to be below the detection limit of the instrument. Because of this, a percent deviation of 100% was found and a t-test was unable to be calculated for the two chemicals' 1st percentile concentration.

Determination of Variance

To ascertain the precision of the instrument, the relative standard deviation (%RSD) was calculated based on the mean and standard deviation of the 10 replicate samples. Variability was determined within the 10 replicate samples at each concentration level. In Figure 4-4, the %RSD is plotted.

Results showed that 97% (74 of 76) of the replicate samples analyzed at the top 4 percentile level had less then 25% variability between the sample mean of the 10 replicate samples and the known concentration. As with the accuracy of the instrument, the lowest two percentile concentrations showed more variability between replicate samples with 47% (18 of 38) of the samples analyzed having less then 25% variability between the sample mean of the 10 replicate samples and the known concentration.

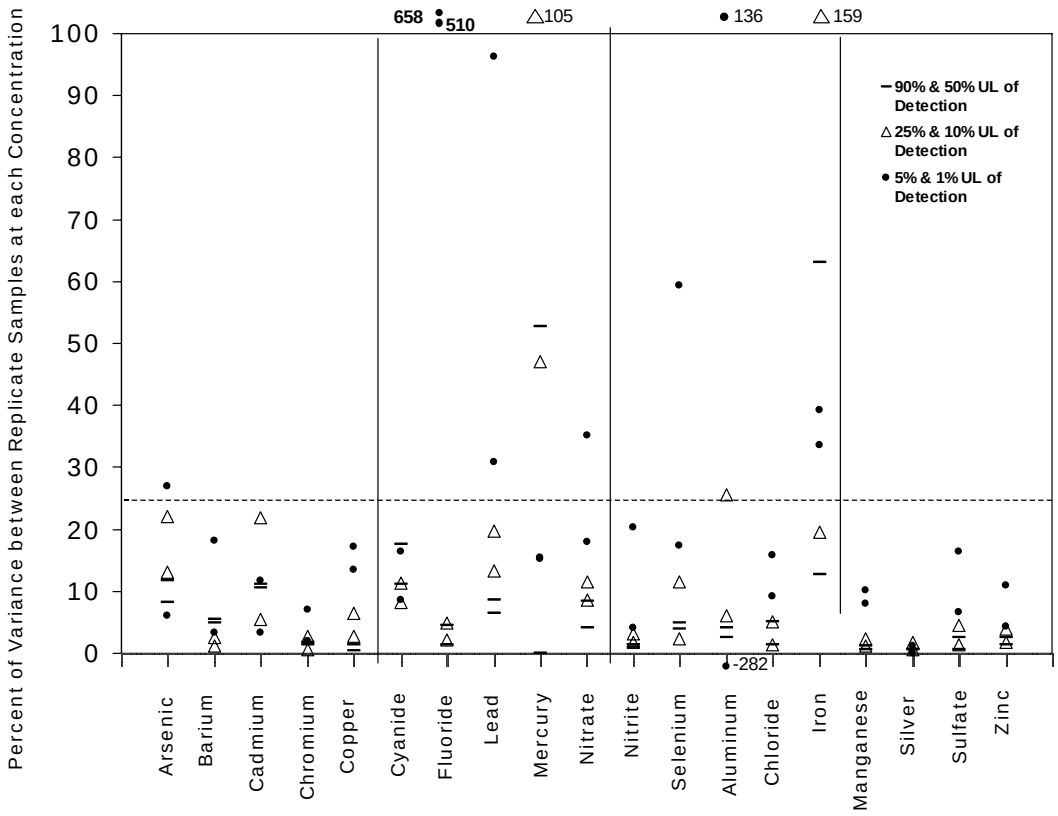

Figure 4-4. Relative Standard Deviation at Six Concentrations.

HACH Unicell Method

The HACH Unicell Detection method is designed for simplified sample preparation compared to the traditional HACH methods used in most of this research. The Unicell method is a test tube-like sample cell designed to analyze water samples using less initial sample few analysis procedures. The water sample is added directly into the Unicell and reacts with reagent prepackaged within the cell. The advantage is faster analysis and less waste but the results are not as accurate or precise. Table 4-5shows a comparison of two HACH Unicell methods Cadmium and Nitrate in comparison to the

corresponding traditional HACH methods. For cadmium, the Unicell calculated lower limit is much higher than the EPA MCL while the calculated lower limit for the traditional method is lower. For nitrate, the Unicell calculated lower limit and the calculated lower limit for the traditional method are both below the EPA MCL. This implies that the easier to use Unicell method may be an effective substitute to the traditional method for nitrate but the cadmium Unicell is not feasible to test down to the EPA standards for cadmium.

	Cadmium	Nitrate
Unicell MDL (ug/ml)	0.400	0.1
Traditional MDL (ug/ml)	0.003	0.2
EPA MCL (ug/ml)	0.020	10
Unicell Variability (%RSD)		

Figure 4-5. Comparison of Calculated MDL / HACH EDL / EPA MCL for Unicell and corresponding traditional methods.

Determination of Usability

Three parameters relating to the usability of the instrument for use by the military in field settings were examined for each contaminant listed on the EPA's primary and secondary drinking water standards. The amount of sample required per analysis, the amount of hazardous waste generated per sample, and the time required for analysis of each sample.

Data gathered for the amount of initial sample required for analysis of each contaminant showed a general trend towards contaminants on the primary standard requiring greater initial sample volumes than those contaminants listed on the secondary standard. Note that the Unicell method for cadmium and nitrate require less sample to conduct the analysis compared to the traditional methods.

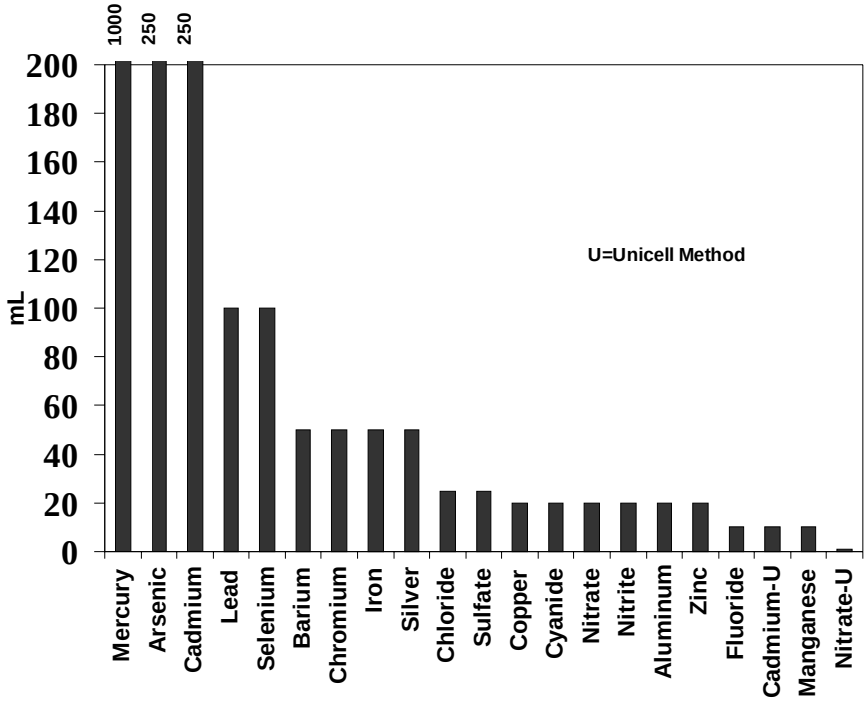

Figure 4-6. Initial Sample Requirements per Sample

Data collected for amounts of hazardous waste generated per sample showed that contaminants requiring separation or extraction of the analyte produced the largest amounts hazardous waste. Figure 4-6 represents the amount of waste generated per sample. For chemicals with no waste per sample depicted, the analytical procedure used generates wastes that are not classified as hazardous wastes by the Federal Resource Conservation Recovery Act (RCRA) and can be flushed down the drain directly or after some type of treatment (i.e. neutralizing waste to a pH of 7, prior to flushing down the drain (HACH, 2003)). The cadmium and nitrate Unicell methods generated less hazardous waste than the corresponding traditional methods.

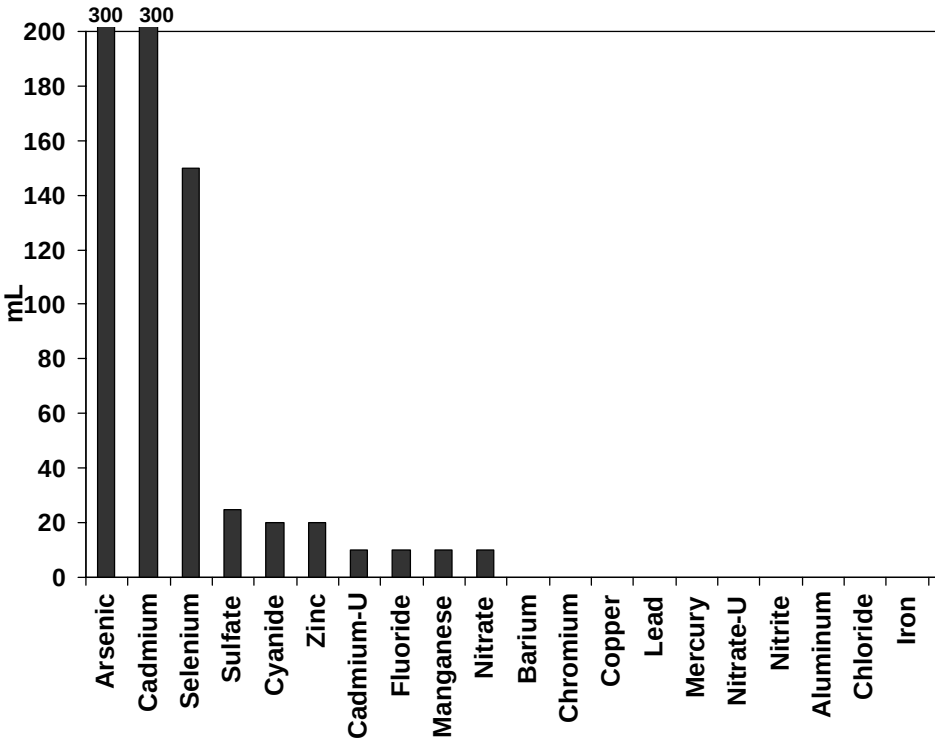

Figure 4-7. Hazardous Waste Generated per Sample

The final parameter in examining the usability of the instrument was the required analysis time per sample. As with the amount of hazardous waste generated, those contaminants requiring procedures to separate or extract the analyte from the water sample required the most time for analysis of the sample. No trends were seen when comparing the Unicell methods against the corresponding traditional reagent methods for cadmium and nitrate. Time durations per sample are depicted in Figure 4-8, showing the longest and shortest time required to complete the analysis for the respective contaminant. The time duration includes time required for sample preparation, analysis steps, and cleaning of lab supplies.

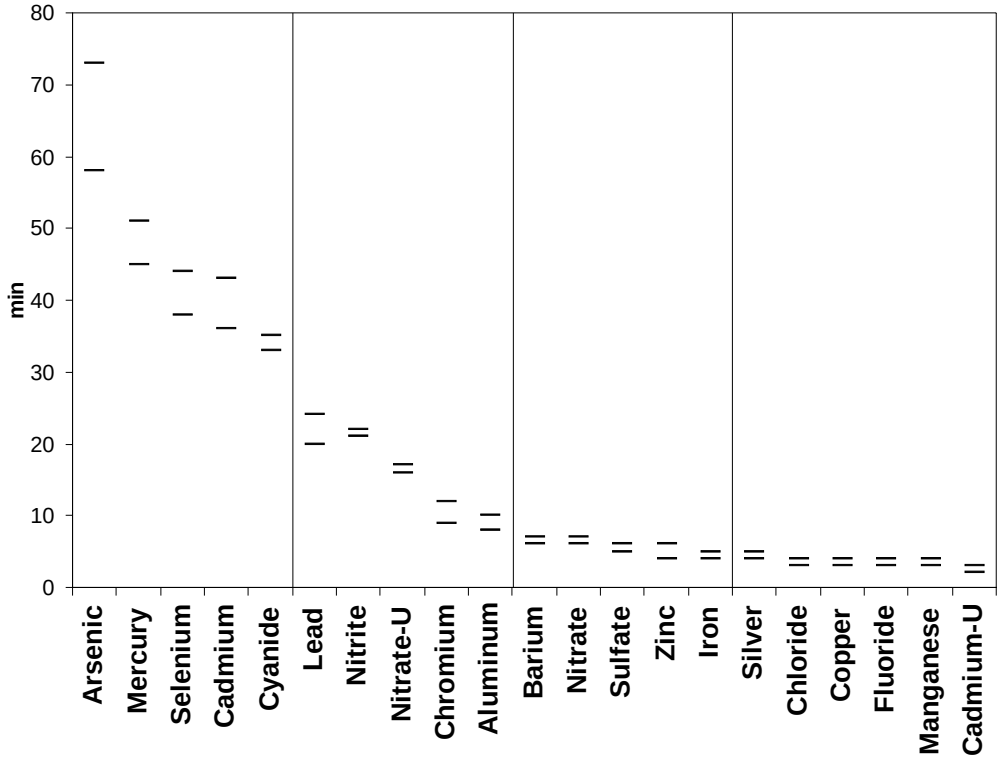

Figure 4-8. Maximum and minimum time durations per sample analyzed.

CHAPTER 5

Discussion

Several of the calculated lower limits were higher than the HACH lower limits as shown in Figure 4-1 and 4-2. However both detection limits were substantially below the EPA's drinking water standard as shown in Figure 4-1 and 4-2. This is an important because it demonstrates the instrument is capable of detecting all inorganic chemicals below the EPA safe drinking water standard. This is especially noteworthy in that the calculated lower limits are not based on the mean but on the upper 99% confidence limit from 10 replicates.

Besides having a detection limit below the EPA safe drinking water standards, the instrument is demonstrated to be relatively precise and accurate. The precision (variability) is relatively low for the four highest concentrations tested but the precision became more erratic at the lower two concentrations tested. Also the accuracy was reasonable. As detailed in most of Appendix C, the confidence intervals did not deviate substantially from the known concentrations. Based on data obtained from the study, results indicate that the DR/4000 UV/Vis spectrophotometer can adequately detect concentrations of contaminants listed on the primary and secondary drinking water standards below regulatory limits and with reasonable accuracy and precision.

Recommendations

The results obtained from this study are applicable to the DR/4000 as it was used in a lab setting. It is highly likely that the variability and therefore the detection limits will increase in a field environment. Further studies would be needed to measure the differences between lab and field sampling. The DR/4000 would be difficult to use in a

field setting. For instance, samples in the study were all measured using a certified balance to ensure that measurements were consistent throughout the study. The balance allows closer accuracy in measuring water and reagent volumes. The instrument was also maintained at its optimal operating temperature and in a clean dry environment without excessive dirt, dust, and debris. A study using the DR/4000 and executing HACH analysis methods in a field setting, would be necessary to assess its performance in this environment.

A comparison study between the HACH Unicell, AccuVac Ampul, and traditional sample cell methods would potentially offer alternative sampling procedures for military field settings if the two previous methods prove to be as accurate as the regular sample cell method. However, the Unicell and AccuVac methods are not available for all contaminants on the EPA's drinking water standards (only 10 Unicell methods and 6 AccuVac methods are available for the 19 contaminants) and some lower limits provided by the manufacturer for these methods are above the EPA's MCL.

Limitations of the Study

HACH Methods used in the study have variations inherent to the methods themselves, affecting the accuracy and precision of analysis. Many methods require the use of reagent and buffer powder pillows (a pouch with powder) and it is very difficult to ensure that all the powder was added to each sample. Care needs to be taken to ensure that losses do not occur.

Mixing of the reagent and buffer powders may also cause variability in analysis. Many analysis procedures require the dissolving of reagent or buffer powders into sample solutions by means of swirling or shaking sample cells. Differences in how completely a

powder dissolves from one sample solution to another sample solution also creates variability in analysis results. These procedural issues may introduce variability between operators.

This study was conducted with one instrument and one skilled operator using deionized water. Several instruments and several operators using a different water matrix would undoubtedly increase variability and detection limits. However it is promising the calculated lower limits in this study were well enough below the EPA MCLs that some degree of added variability may be tolerable.

Discussion on Usability of Instrument in a Field Setting

Because of necessary reagents and solvents associated with the sampling procedures, lab equipment, safety equipment, and hazardous materials associated with the analysis of contaminants, the DR/4000 would be most practical for use on extended or long-term deployments in a climate-controlled environment. The instrument requires stable temperatures and a clean analysis environment with good logistical support, and unlimited access to potable water supplies for cleaning lab supplies.

Many procedures require the use delicate glassware (i.e. distillation apparatus, cold vapor separation apparatus, absorbing columns) to complete the analysis of water samples. Many of the procedures use reagents and solvents that are highly corrosive, caustic, or flammable. Reagents and solvents used in many of the HACH procedures are classified as eye, skin, or inhalation hazards and require the use of engineering controls (i.e. fume hood) and the use of personal protective equipment.

Another aspect impacting the usability of the DR/4000 in a field setting is the generation of hazardous waste from analysis procedures. Several analytical procedures

produce substantial quantities of hazardous wastes that can be harmful if mishandled. The use of the HACH's Unicell or AccuVac sampling methods may offer an alternative to the procedures requiring engineering controls or the use of safety equipment.

Required lab supplies, safety equipment, and hazardous materials all impact on the usability of the DR/4000 in a military field setting, however, conscientious safety and hazardous waste management programs, along with good lab practices, can reduce the risks associated with the analytical procedures.

Conclusion

The HACH DR/4000 has demonstrated that it can accurately detect inorganic contaminants listed on the EPA's primary and secondary drinking water standards below the regulatory limits. The accuracy and variability are reasonable for this type of instrument. This instrument could be valuable for analyzing military field drinking water to EPA standards in a long-term deployment situation with a controlled environment.

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APPENDIX A

CALCULATED LOWER LIMITS

Contaminant	HACH Estimated Lower Limit (mg/L)	Calculated Lower Limit (mg/L)	Percent Deviation (%)
Arsenic - (As)	not provided	0.0286*	N/A
Barium - (Ba)	not provided	1.2*	N/A
Cadmium - (Cd)	0.0013	0.0008	-37.6923
Cadmium-Unicell - (Cd-(U))	0.0200	0.0754	276.8000
Chromium - (Cr)	0.0030	0.0028	-5.5333
Copper - (Cu)	0.0210	0.0280	33.3333
Cyanide - (Cn)	0.0030	0.0038	27.0000
Fluoride - (Fl)	0.0200	0.1000	400.0000
Lead - (Pb)	0.0020	0.0060	200.0000
Mercury - (Hg)	0.0001	0.0002	71.3000
Nitrate - (NO3-)	0.1000	0.0100	-90.0000
Nitrate-Unicell - (NO3- -(U))	0.2000	0.3000	50.0000
Nitrite - (NO2- (N-))	0.0008	0.0098	1125.0000
Selenium - (Se)	0.0030	0.0170	466.6667
Aluminum - (Al)	0.0020	0.0170	650.0000
Chloride - (Cl)	0.2400	0.240**	0.0000
Iron - (Fe)	0.0250	0.0240	-4.0000
Manganese - (Mn)	0.0050	0.0020	-60.0000
Silver - (Ag)	0.0060	0.0040	-33.3333
Sulfate - (SO4)	not provided	0.9500	N/A
Zinc - (Zn)	0.0090	0.0409	354.0000

APPENDIX B

DESCRIPTIVE STATISTICS

Contaminant	Percentile	Conc. (mg/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
Arsenic	90%	0.180	0.1730	0.00448	0.1629	0.1831	0.04	0.01418
	50%	0.100	0.1070	0.0040	0.0980	0.1160	0.03	0.01252
	25%	0.050	0.0690	0.0048	0.0581	0.0799	0.05	0.01524
	10%	0.020	0.0179	0.0007	0.0162	0.0196	0.01	0.00233
	5%	0.010	0.0116	0.0002	0.0111	0.0121	0.00	0.00070
	1%	0.002	0.0052	0.0004	0.0042	0.0062	0.00	0.00140
Barium	Percentile	Conc. (mg/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
	90%	90.000	93.300	1.5573	89.777	96.823	13.7	4.9248
	50%	50.000	47.960	0.7790	46.200	49.720	6.7	2.4600
	25%	25.000	29.520	0.1960	29.077	29.963	1.9	0.6197
	10%	10.000	10.990	0.0379	10.904	11.076	0.3	0.1197
	5%	5.000	5.330	0.0517	5.213	5.447	0.6	0.1636
	1%	1.000	0.850	0.0522	0.732	0.968	0.4	0.1650
Cadmium	Percentile	Conc. (mg/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
	Unicell.08	0.08	0.083000	0.0206510	0.058906	0.107094	0.1200	0.0336815
	Unicell.15	0.15	0.154000	0.0073333	0.137411	0.170589	0.0700	0.0231900
	90%	0.072	0.045000	0.0015129	0.041578	0.048422	0.0120	0.0047842
	50%	0.040	0.022200	0.0007860	0.020422	0.023978	0.0060	0.0024855
	25%	0.020	0.015300	0.0002603	0.014711	0.015889	0.0030	0.0008233
	10%	0.008	0.011400	0.0007916	0.009609	0.013191	0.0070	0.0025033
	5%	0.004	0.007700	0.0000792	0.007561	0.007919	0.0006	0.0002503
	1%	0.001	0.004500	0.0001667	0.004123	0.004877	0.0010	0.0005270
Chromium	Percentile	Conc. (mg/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
	90%	0.630	0.65490	0.003588	0.64678	0.66302	0.036	0.011348
	50%	0.350	0.37510	0.001650	0.37137	0.37883	0.018	0.005216
	25%	0.175	0.19300	0.000333	0.19225	0.19375	0.003	0.001054
	10%	0.070	0.08110	0.000657	0.07961	0.08259	0.005	0.002079
	5%	0.035	0.04260	0.000267	0.04200	0.04320	0.003	0.000843
	1%	0.007	0.01220	0.000291	0.01154	0.01286	0.003	0.000919
Copper	Percentile	Conc. (mg/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
	90%	1.170	1.17680	0.001104	1.17430	1.17930	0.010	0.003490
	50%	0.658	0.65800	0.002720	0.65185	0.66415	0.029	0.008602
	25%	0.332	0.33190	0.002838	0.33548	0.33832	0.030	0.008975
	10%	0.131	0.13080	0.002695	0.12470	0.13690	0.030	0.008522
	5%	0.075	0.07540	0.003215	0.06813	0.08267	0.033	0.010167
	1%	0.015	0.01520	0.000841	0.01330	0.01710	0.009	0.002658
Cyanide	Percentile	Conc. (mg/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
	90%	0.216	0.17820	0.009975	0.15563	0.20077	0.095	0.031545
	50%	0.120	0.11510	0.004037	0.10597	0.12423	0.045	0.012767
	25%	0.060	0.05060	0.001821	0.04648	0.05472	0.016	0.005758
	10%	0.024	0.02550	0.000654	0.02402	0.02698	0.006	0.002068
	5%	0.012	0.01360	0.000371	0.01276	0.01444	0.003	0.001174
	1%	0.002	0.00500	0.000258	0.00442	0.00558	0.003	0.000816

* MDL calculated from average of the 5th and 1st percentiles

** MDL calculated at concentration of HACH EDL

(U) – Unicell Method

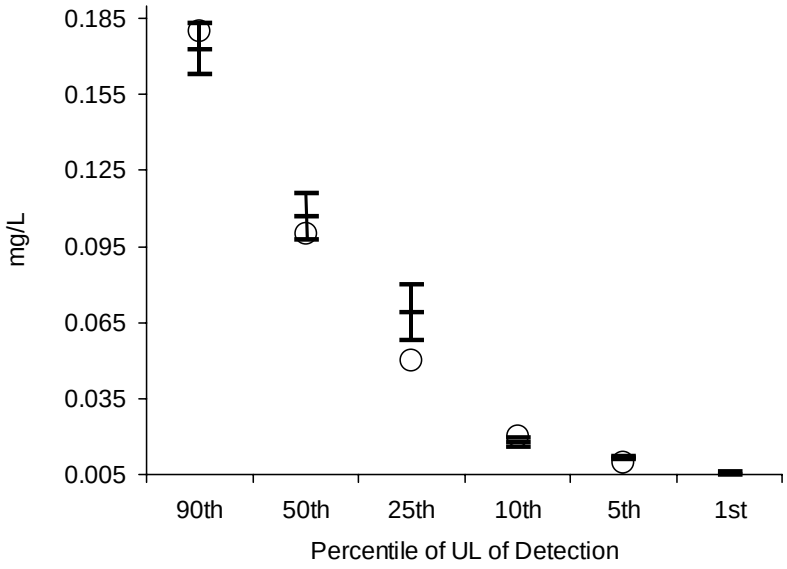
	Percentile	Conc. (mg/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
Fluoride	90%	1.80	2.0640	0.02956	1.9971	2.1309	0.34	0.09348
	50%	1.00	1.0600	0.00482	1.0481	1.0699	0.04	0.01524
	25%	0.50	0.5950	0.00401	0.5859	0.6041	0.05	0.01269
	10%	0.20	0.2280	0.00359	0.2199	0.2361	0.03	0.01135
	5%	0.10	0.0060	0.00968	-0.0159	0.0279	0.07	0.03062
	3%	0.05	0.1280	0.00389	0.1192	0.1368	0.04	0.01229
	1%	0.02	0.0020	0.00416	-0.0074	0.0114	0.04	0.01317
	Percentile	**Conc. (mg/L)**	**Mean**	**Std. Error**	**95% CI for Mean (Lower)**	**95% CI for Mean (Upper)**	**Range**	**SD**
Lead	90%	135	158.60	3.229	151.30	165.90	31	10.211
	50%	75	96.00	2.599	90.12	101.88	28	8.219
	25%	38	39.40	2.468	33.82	44.98	21	7.806
	10%	15	12.40	0.521	11.22	13.58	5	1.647
	5%	8	6.90	0.674	5.38	8.42	7	2.132
	1%	2	3.90	1.187	1.21	6.59	12	3.755
	Percentile	**Conc. (ug/L)**	**Mean**	**Std. Error**	**95% CI for Mean (Lower)**	**95% CI for Mean (Upper)**	**Range**	**SD**
Mercury	90%	2.250	1.250	0.0000543	0.001127	0.001373	0.0005	0.0001716
	50%	1.250	0.710	0.0000348	0.000631	0.000789	0.0003	0.0001101
	25%	0.625	0.110	0.0000233	0.000057	0.000163	0.0002	0.0000738
	10%	0.250	0.050	0.0000167	0.000012	0.000088	0.0001	0.0000527
	5%	0.125	0.080	0.0000133	0.000050	0.000110	0.0001	0.0000422
	1%	0.025	0.000	0.0000000	0.000000	0.000000	0.0000	0.0000000
	Percentile	**Conc. (mg/L)**	**Mean**	**Std. Error**	**95% CI for Mean (Lower)**	**95% CI for Mean (Upper)**	**Range**	**SD**
Nitrate	90%	4.50	4.100	0.0516	3.983	4.217	0.5	0.1633
	50%	3.50	2.960	0.0806	2.778	3.142	0.8	0.2547
	25%	1.25	1.230	0.0335	1.154	1.306	0.3	0.1059
	Unicell @25%	1.25	5.670	0.0335	5.594	5.746	0.3	0.1059
	10%	0.50	0.490	0.0180	0.449	0.531	0.2	0.0568
	5%	0.10	0.270	0.0153	0.235	0.305	0.1	0.0483
	1%	0.05	0.100	0.0000	0.000	0.000	0.0	0.0000
	Percentile	**Conc. (ug/L)**	**Mean**	**Std. Error**	**95% CI for Mean (Lower)**	**95% CI for Mean (Upper)**	**Range**	**SD**
Nitrite	90%	0.270	0.283500	0.0009551	0.281339	0.285661	0.0107	0.0030203
	50%	0.150	0.152240	0.0006391	0.150794	0.153686	0.0069	0.0020211
	25%	0.075	0.072770	0.0004115	0.071839	0.073701	0.0043	0.0013013
	10%	0.030	0.026030	0.0002612	0.025439	0.026621	0.0024	0.0008260
	5%	0.015	0.013270	0.0001693	0.012887	0.013653	0.0016	0.0005355
	1%	0.003	0.003650	0.0002349	0.003119	0.004181	0.0026	0.0007427
	Percentile	**Conc. (ug/L)**	**Mean**	**Std. Error**	**95% CI for Mean (Lower)**	**95% CI for Mean (Upper)**	**Range**	**SD**
Selenium	90%	0.90	0.66830	0.008179	0.64980	0.68680	0.077	0.025863
	50%	0.50	0.39260	0.005982	0.37907	0.40613	0.057	0.018916
	25%	0.25	0.23830	0.001770	0.23429	0.24231	0.016	0.005599
	10%	0.10	0.10350	0.003778	0.09459	0.11205	0.035	0.011947
	5%	0.05	0.05970	0.003313	0.05220	0.06720	0.036	0.010478
	1%	0.01	0.00870	0.001633	0.00501	0.01239	0.014	0.005165

	Percentile	Conc. (ug/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
Aluminum	90%	0.225	0.20840	0.001648	0.20467	0.21213	0.017	0.005211
	50%	0.125	0.12940	0.001714	0.12552	0.13328	0.019	0.005420
	25%	0.063	0.07180	0.001397	0.06864	0.07496	0.012	0.004417
	10%	0.025	0.02470	0.002006	0.02016	0.02924	0.019	0.006343
	5%	0.013	0.00490	0.002111	0.00013	0.00967	0.018	0.006674
	1%	0.003	-0.00190	0.001696	-0.00570	0.00194	0.012	0.005363
	Percentile	Conc. (ug/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
Chloride	90%	22.50	24.9460	0.43039	23.8620	25.8469	4.18	1.25129
	50%	12.50	12.8150	0.05999	12.6994	12.9761	0.56	0.18435
	25%	6.25	6.3370	0.11206	6.0738	6.5906	1.10	0.31732
	10%	2.50	2.8978	0.01211	2.8699	2.9257	0.05	0.03632
	5%	1.25	1.5778	0.04960	1.4634	1.6922	0.49	0.14881
	1%	0.25	0.4822	0.02521	0.4241	0.5404	0.25	0.07563
	Percentile	Conc. (ug/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
Iron	90%	1.620	1.25050	0.058162	1.11893	1.38207	0.526	0.183925
	50%	0.900	0.90870	0.007194	0.89243	0.92497	0.069	0.022750
	25%	0.450	0.49590	0.006420	0.48138	0.51042	0.066	0.020300
	10%	0.180	0.16210	0.014817	0.12858	0.19562	0.160	0.046855
	5%	0.090	0.10800	0.002329	0.10273	0.11327	0.018	0.007364
	1%	0.019	0.03620	0.000975	0.03399	0.03841	0.008	0.003084
	Percentile	Conc. (ug/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
Manganese	90%	0.630	0.58040	0.002891	0.57237	0.58843	0.016	0.006465
	50%	0.350	0.32580	0.000800	0.32358	0.32802	0.004	0.001789
	25%	0.175	0.16560	0.000812	0.16334	0.16786	0.005	0.001817
	10%	0.070	0.06880	0.000735	0.06676	0.07084	0.004	0.001643
	5%	0.035	0.04000	0.001449	0.03598	0.04402	0.009	0.003240
	1%	0.007	0.00760	0.000400	0.00649	0.00871	0.002	0.000894
	Percentile	Conc. (ug/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
Silver	90%	0.630	0.64230	0.001248	0.63948	0.64512	0.010	0.003945
	50%	0.350	0.35690	0.000567	0.35562	0.35818	0.005	0.001792
	25%	0.175	0.18390	0.000379	0.18304	0.18476	0.003	0.001197
	10%	0.070	0.06630	0.000367	0.06547	0.06713	0.003	0.001160
	5%	0.035	0.03320	0.000133	0.03290	0.03350	0.001	0.000422
	1%	0.007	0.00440	0.000267	0.00380	0.00500	0.002	0.000843
	Percentile	Conc. (ug/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
Sulfate	90%	63.0	67.4830	0.13241	67.1835	67.7825	1.20	0.41870
	50%	35.0	40.7660	0.32452	40.0319	41.5001	3.53	1.02621
	25%	17.5	21.1990	0.09287	20.9889	21.4091	0.82	0.29369
	10%	7.0	6.5810	0.09268	6.3713	6.7907	0.90	0.29309
	5%	3.5	2.0010	0.04252	1.9048	2.0972	0.37	0.13445
	1%	0.7	0.2190	0.01140	0.1932	0.2448	0.12	0.03604
	Percentile	Conc. (ug/L)	Mean	Std. Error	95% CI for Mean (Lower)	95% CI for Mean (Upper)	Range	SD
Zinc	90%	2.70	2.59720	0.021082	2.54951	2.64489	0.189	0.066668
	50%	1.50	1.55120	0.006475	1.53655	1.56585	0.072	0.020477
	25%	0.75	0.78280	0.004289	0.77310	0.79250	0.044	0.013563
	10%	0.30	0.32820	0.003969	0.31922	0.33718	0.029	0.012550
	5%	0.15	0.15720	0.002149	0.15234	0.16206	0.018	0.006795
	1%	0.03	0.03440	0.001176	0.03174	0.03706	0.013	0.003718

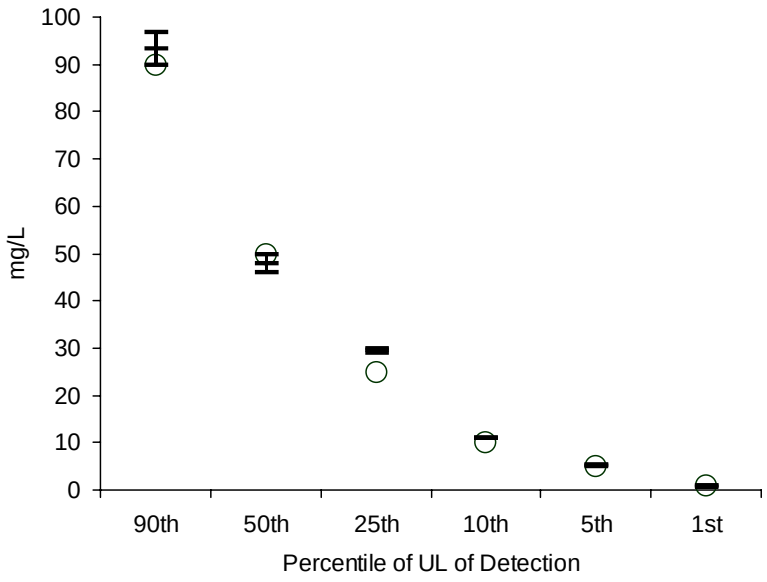
APPENDIX C

95% CONFIDENCE INTERVALS

The 95% confidence interval for the mean at each percentile concentration was constructed for each contaminant on the EPA's primary and secondary standards. The circle on each graph represents the standard concentration and the bars with dashes represent mean and the 95% confidence interval.



95th CI for Arsenic



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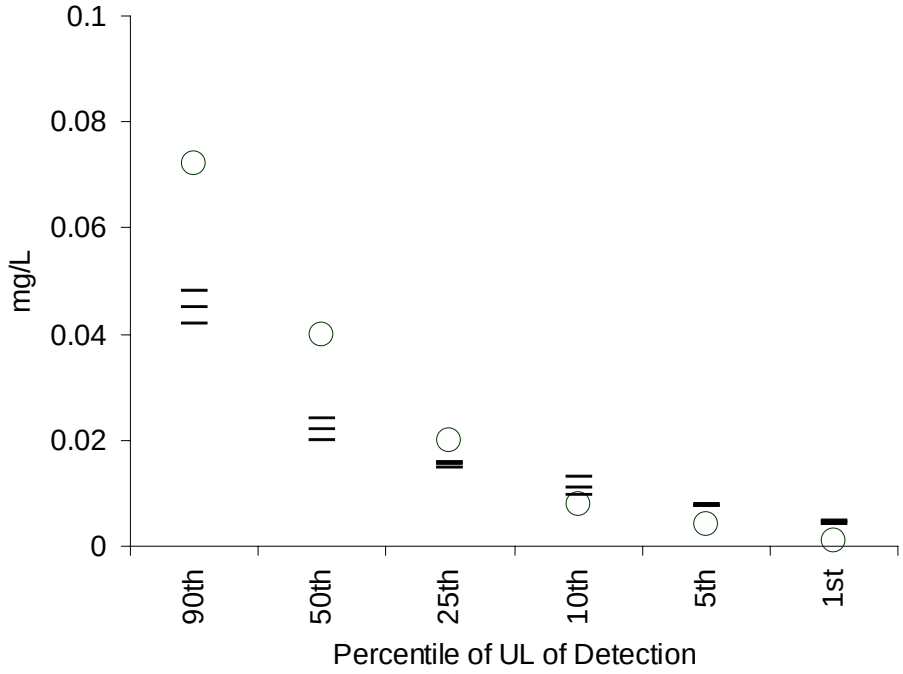
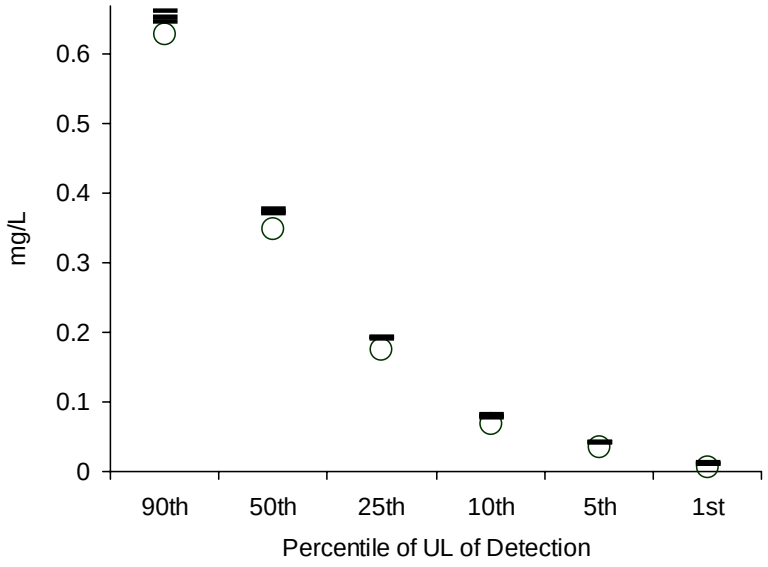
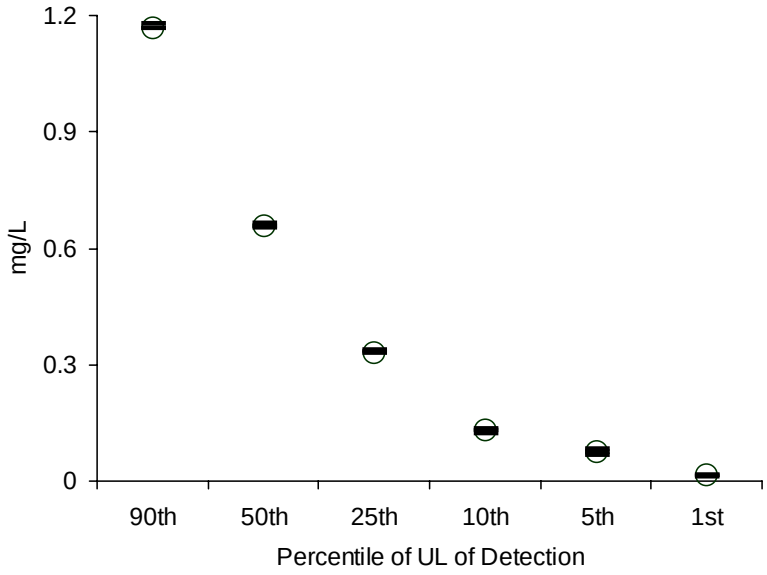


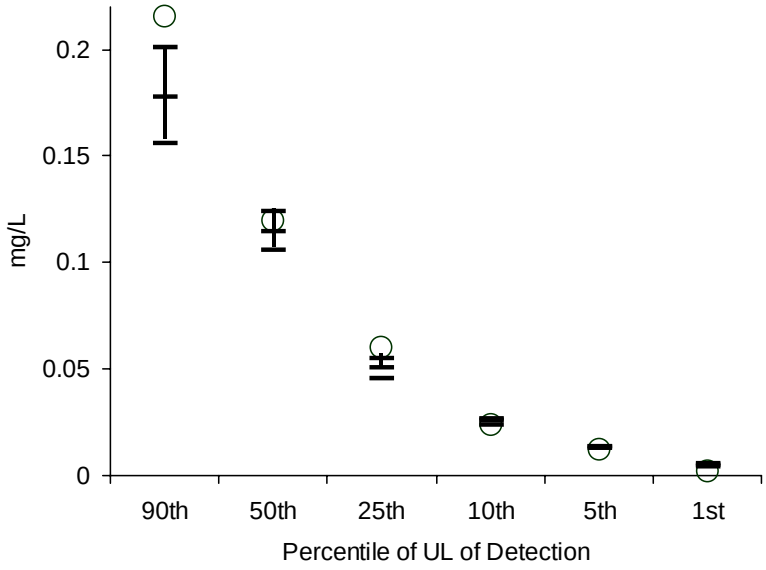
95% CI for Cadmium



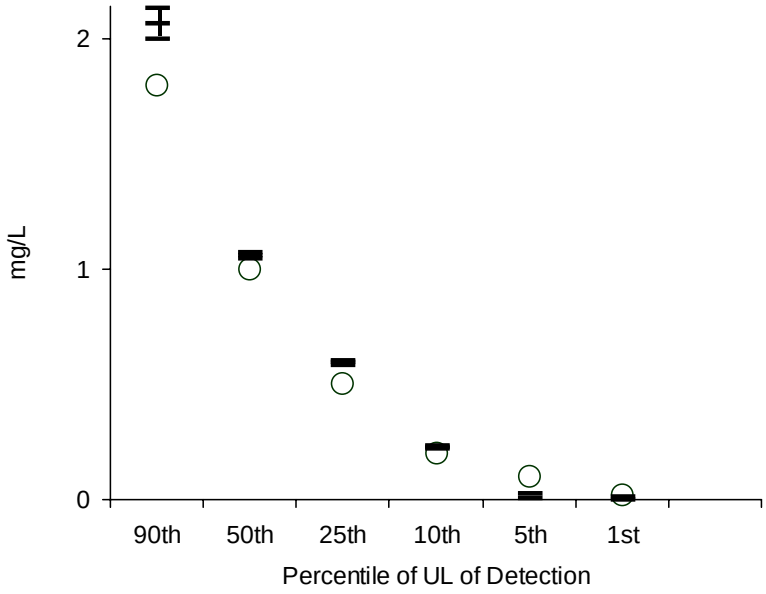
95% CI for Chromium



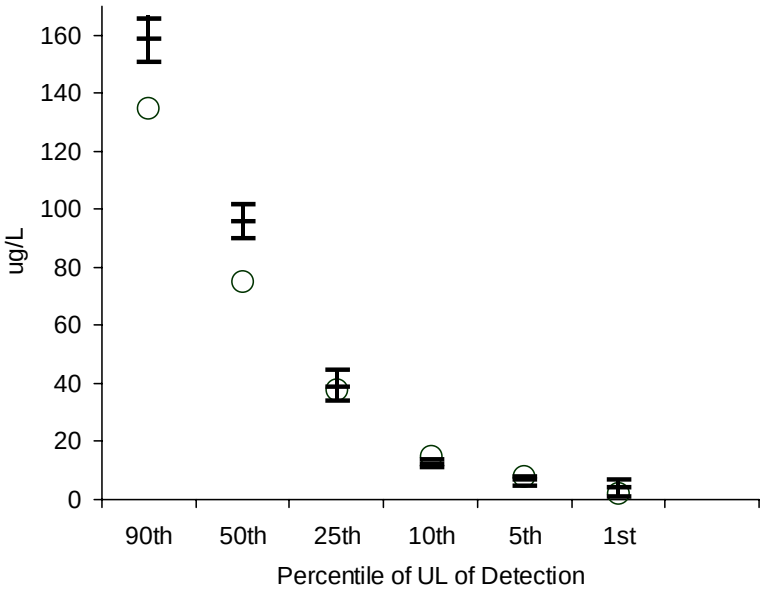
95% CI for Copper



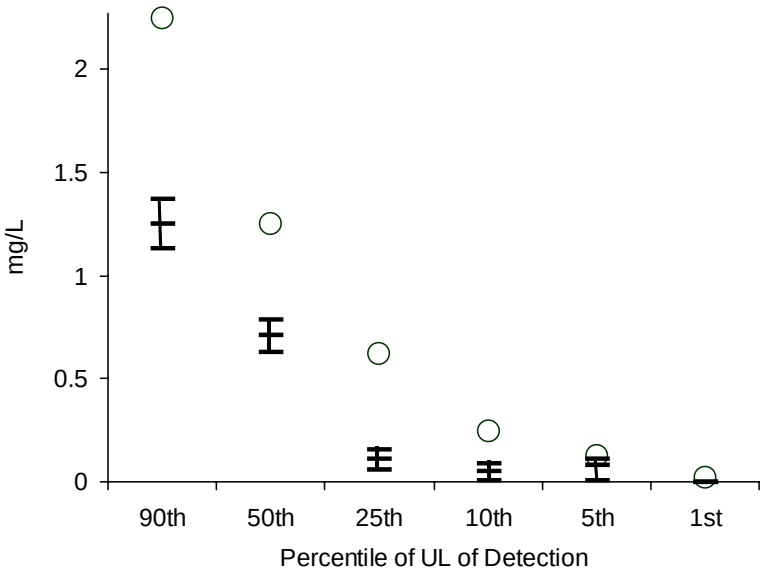
95% CI for Cyanide



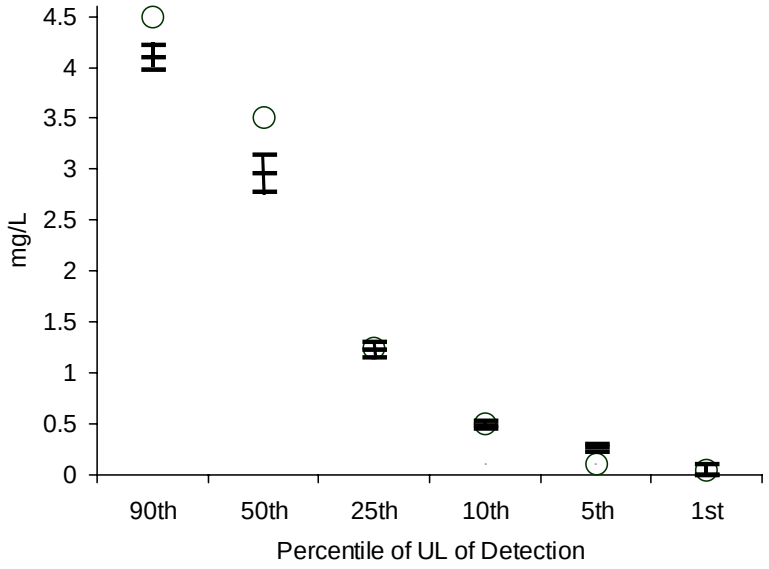
95% CI for Fluoride



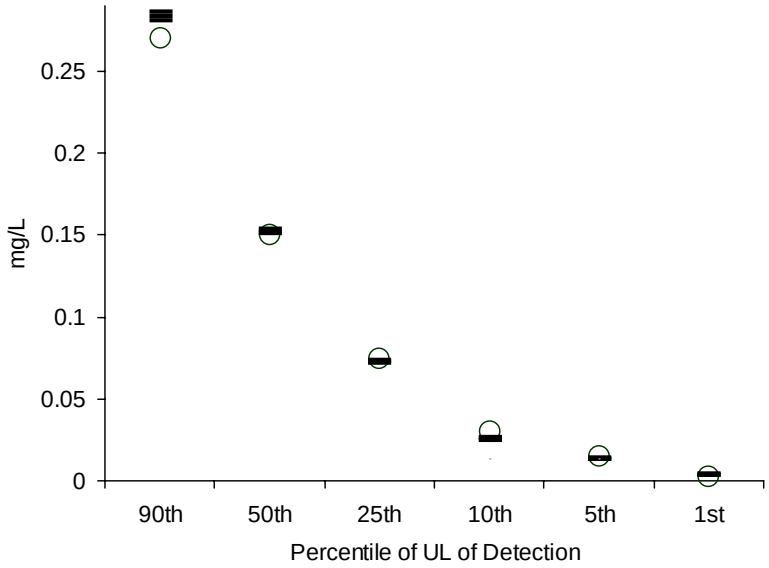
95% CI for Lead



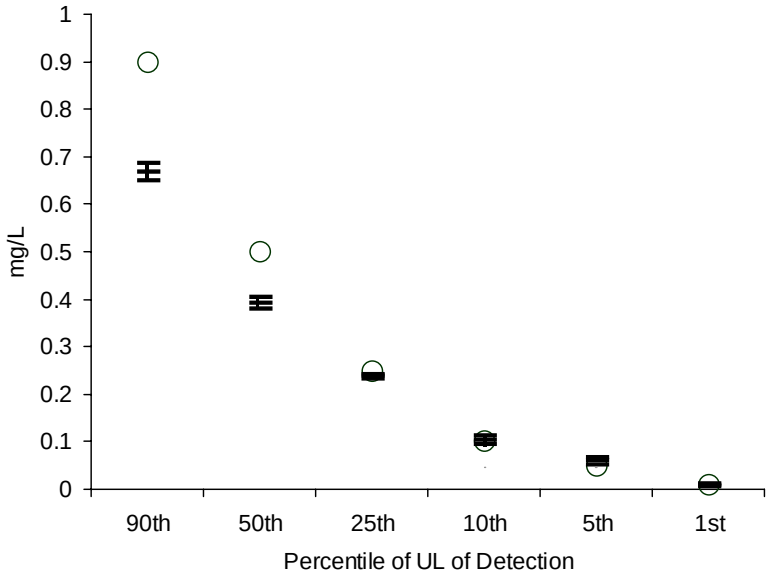
95% CI for Mercury



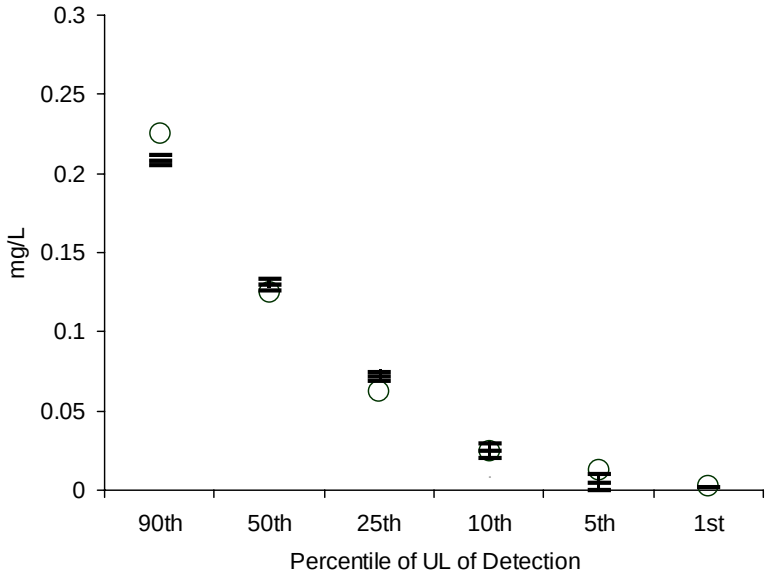
95% CI for Nitrate



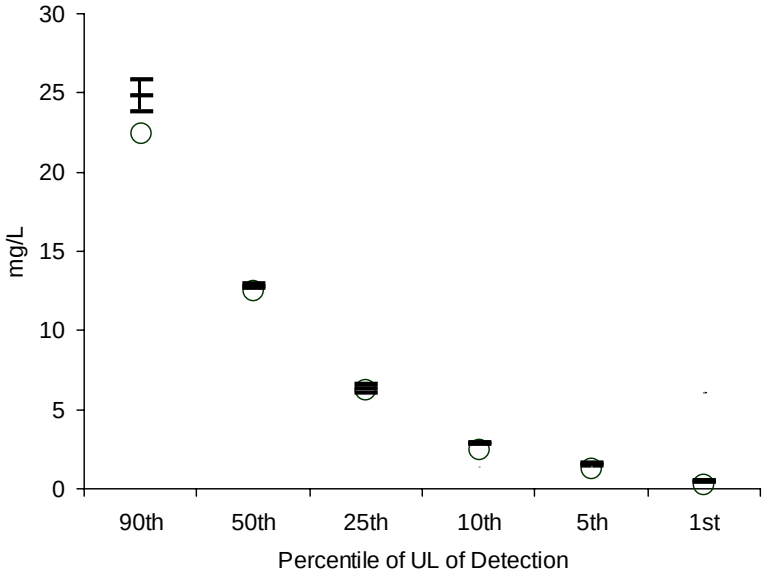
95% CI for Nitrite



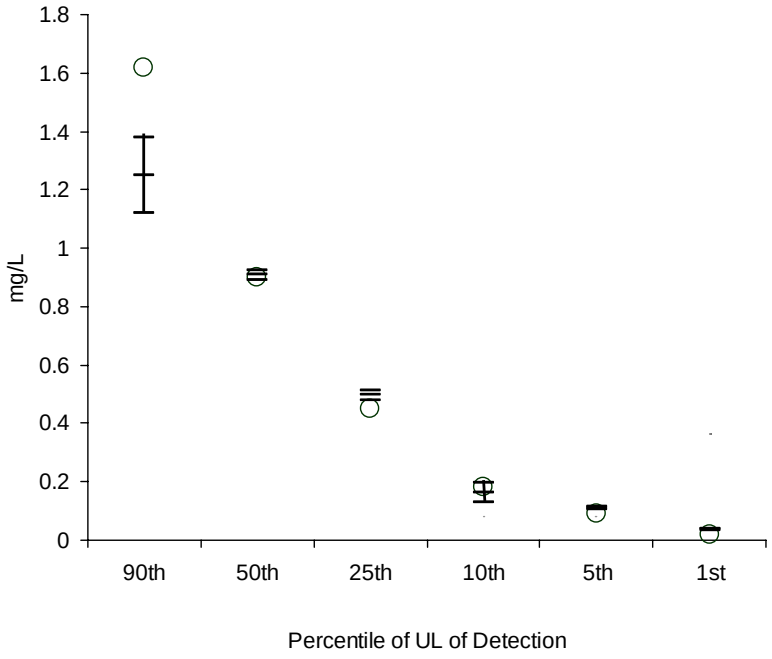
95% CI for Selenium



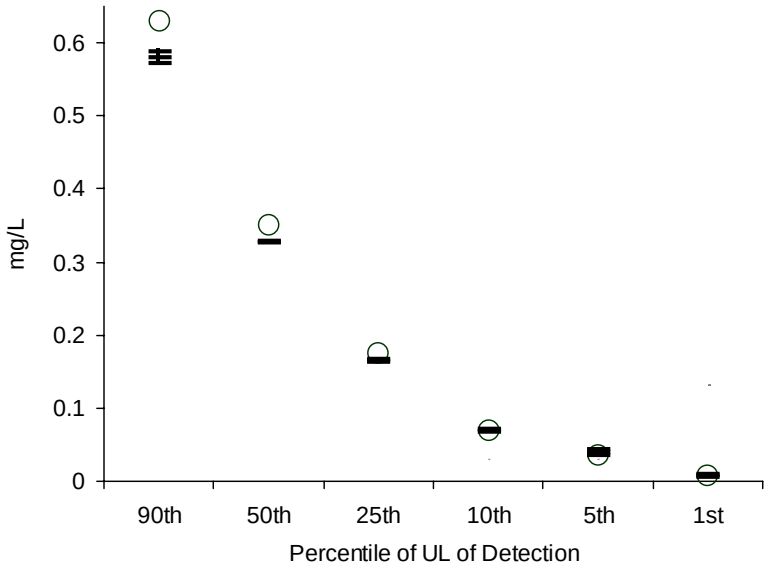
95% CI for Aluminum



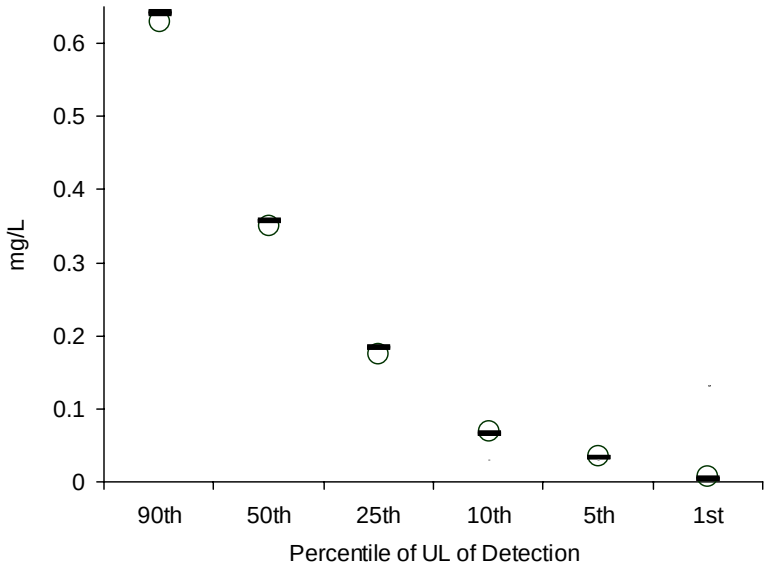
95% CI for Chloride



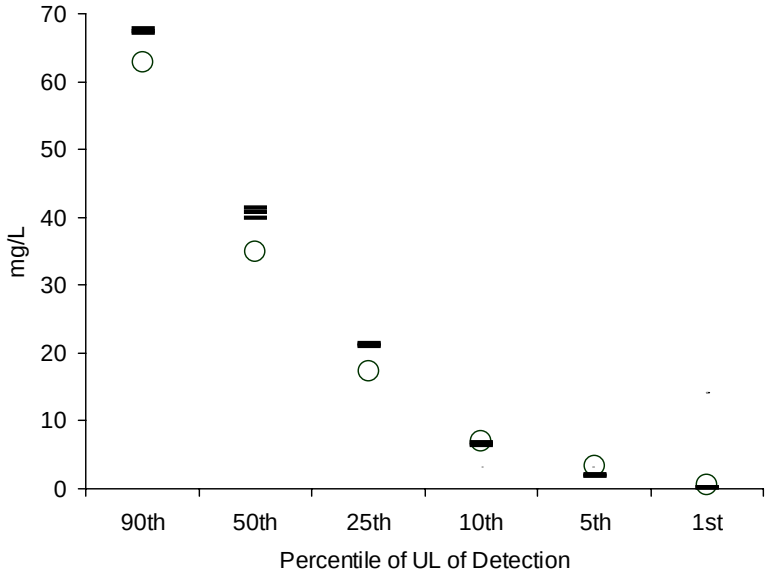
95% CI for Iron



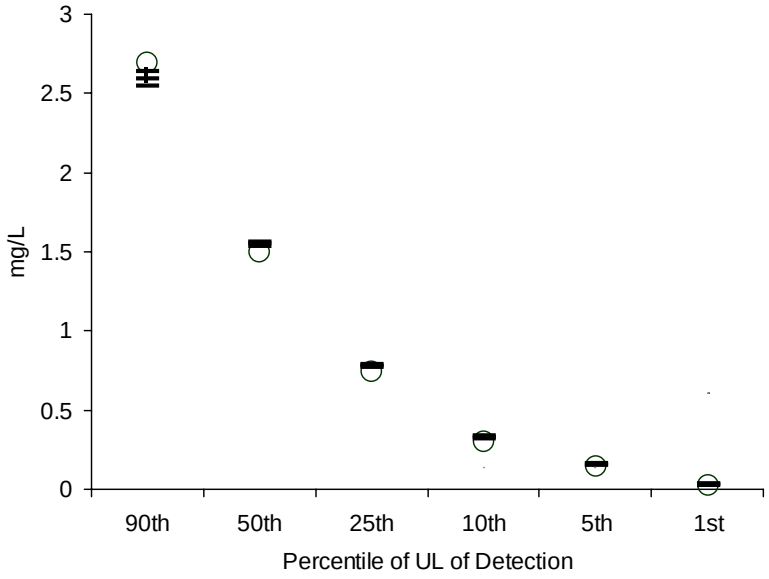
95% CI for Manganese



95% CI for Silver



95% CI for Sulfate



95% CI for Zinc

CURRICULUM VITAE

SCOTT HUNTER NEWKIRK

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DATE & PLACE OF BIRTH: June 19, 1969, Carmel, New York, USA

CIVILIAN EDUCATION:
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MILITARY EDUCATION:
Officer Basic Course, Ft. Sam Houston, Texas, 1994
Principles of Preventive Medicine Course, Ft. Sam Houston, Texas, 1994
Basic Industrial Hygiene Course, APG, Maryland, 1994
Intermediate Industrial Hygiene Course, Ft. Sam Houston, Texas, 1994
Medical Management of Chemical Casualty Course, Ft. Detrick/APG-EA, Maryland, 1996
Officer Advanced Course, Ft. Sam Houston, Texas, 2000
Combined Arms Service Staff School, Ft. Leavenworth, Kansas, 2002

MILITARY POSITIONS HELD:
Student, June 2003-Current, Uniformed Services University of the Health Sciences, Bethesda, MD
Operations Officer, June 2002-June2003, DCSOPS, USACHPPM, APG, Maryland
Commander, Headquarters and Headquarters Company, June 2000-June2002, USACHPPM, APG, Maryland
Environmental Science Officer, November 1998-March 2000, Tripler Army Medical Center, Honolulu, Hawaii
Division Preventive Medicine Officer, December 1996-November 1998, 25th Infantry Division (Light), Schofield Barrack, Hawaii
Industrial Hygiene Project Officer, June 1994-November 1996, USACHPPM-North, Ft. George G. Meade, Maryland

AWARDS AND DECORATIONS:
Meritorious Service Medal (1 Oak Leaf Cluster)
Army Commendation Medical
Navy Achievement Medal
Overseas Service Ribbon
Expert Field Medical Badge
Parachutists Badge
Air Assault Badge
German Troop Duty Proficiency Badge